Supporting Information

Visible-Light-Induced Intramolecular Charge Transfer in the Radical Spirocyclisation of Indole-Tethered Ynones

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General Information

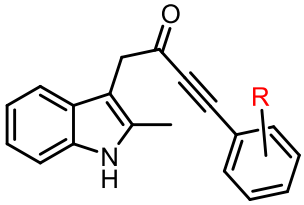
Except where stated, all reagents were purchased from commercial sources and used without further purification. Except where stated, all experimental procedures were carried out under an atmosphere of argon. Except where stated, anhydrous solvents obtained from commercial sources or from an Innovative Technology Inc. PureSolv® solvent purification system were used. Main solvents such as anhydrous 1,2-dichloroethane (DCE) and acetonitrile (MeCN) were supplied by Sigma Aldrich and degassed using argon balloon and stored over activated 3Å molecular sieves. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a JEOL ECX400 or JEOL ECS400 spectrometer, operating at 400 MHz, 100 MHz, and 376 MHz respectively. All spectral data was acquired at 295 K unless otherwise stated. Chemical shifts (δ) are quoted in parts per million (ppm). The residual solvent peas were used as references in ^{1}HNMR: δ_H 7.26 ppm for $CDCl_3$ and 1.95 ppm for CD_3CN. The reference residual peak for $^{13}C\{^{1}H\}$NMR: δ_C 77.0 ppm for $CDCl_3$ and 1.39 ppm for CD_3CN. Coupling constants (J) are reported in Hertz (Hz) to the nearest 0.1 Hz. The multiplicity abbreviations used are: s singlet, d doublet, t triplet, q quartet, td triple doublet, tt triple triplet, dd double doublet, dq double quartet, m multiplet. Signal assignment was achieved by analysis of DEPT, COSY, NOESY, and HMQC experiments where required. Infrared (IR) spectra were recorded on a PerkinElmer UATR 2 spectrometer, either as a compressed solid or neat oil. Mass-spectra (low and high-resolution) were obtained by the University of York Mass Spectrometry Service, using electrospray ionisation (ESI) on a Bruker Daltonics, Micro-Tof spectrometer. UV-Vis spectroscopy was recorded using Shimadzu UV-Vis Spectrophotometer UV-2600 system (See S10) for UV-vis experimental details. Melting points were determined using Gallenkamp apparatus and are uncorrected. Thin layer chromatography was carried out on Merck silica gel 60F_{254} pre-coated aluminium foil sheets and were visualised using UV light (254 nm) and stained with basic aqueous potassium permanganate. Flash column chromatography was carried out using slurry packed Fluka silica gel (SiO_2), 35–70 µm, 60 Å or Fuji Silysia Chromatorex Silica gel (SiO_2), neutral MB100, 75-200 µm, 100 Å under a light positive pressure, eluting with the specified solvent system.

Structures of the products were identified by ^{1}H NMR, $^{13}C\{^{1}H\}$ NMR, ^{19}F NMR, HRMS, IR, melting point (solid at RT) and compared with **13g** (CCDC 1945620), **13k** (CCDC 1945621), **16a** (CCDC 1945619), **16j** (CCDC 1945618), and **16g** (CCDC 1945660), and which were confirmed by X-ray crystallography. Supplementary crystallography data can be downloaded free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

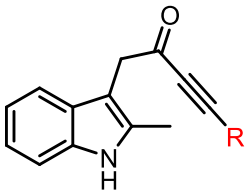
Materials:

The following chemicals were purchased and used as received: 2-methyl-3-indoleacetic acid, 3-indole acetic acid, 5-methoxy-3-indoleacetic acid, 1-methylindole-3-carboxaldehyde, methyl 2-(1H-indol-3-yl)acetate (**SM6**), [4-phenylbut-3-yn-2-one (**20**), diphenylacetylene (**22**), *N*,*O*-dimethylhydroxylamine hydrochloride (MeNHOMe.HCl), phenylacetylene, 4-ethynylanisole, 1-ethynyl-4-fluorobenzene, cyclopropylacetylene, 1,1'-carbonyldiimidazole (CDI), propylphosphonic anhydride solution 50% in EtOAc (T3P®**), Captopril (CAS number: 62571-86-2), α-tocopherol, N-acetyl-*L*-cysteine methyl ester (SM9, CAS number: 7652-46-2),** N-methoxy-N-methyl-2-(2-phenyl-1H-indol-3-yl)acetamide **SM10**. [2a] **Unless stated otherwise, commercially available aryl-/alkyl-/hetero-thiols were used without further purification.** Commercially available photocatalysts were used as received.

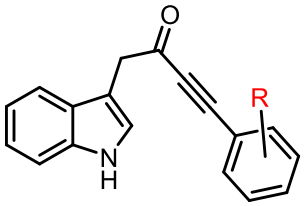
The following compounds are reported. Unless otherwise stated, these compounds were synthesised based on reported methods.



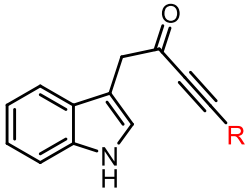
13a, R = H [1]
13b, R = 4-OMe [1]
13c, R = 4-F [1]



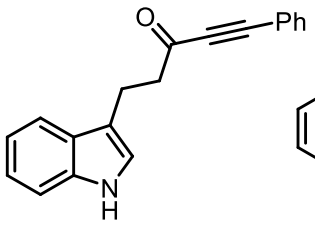
13e, R = C_6H_{13} [1]
13f, R = cyclopropyl [1]



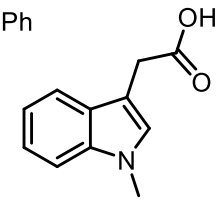
13g, R = H [1]
13h, R = 3,4,5-OMe [1]
13i, R = 4-Br [2a]



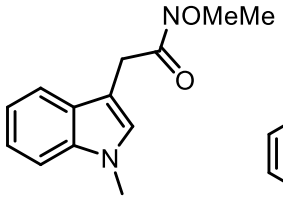
13j, R = cyclopropyl [1]
13m, R = cyclopentyl [2b]
13n, R = $CH_2CH_2CH_2Cl$ [2b]



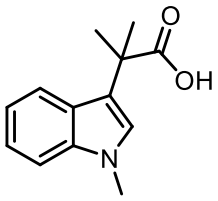
13p [2a]



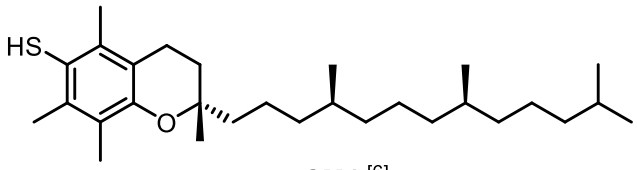
SM1 [3]



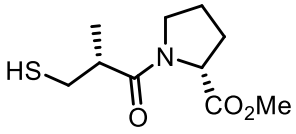
SM2 [4]



SM3 [5]



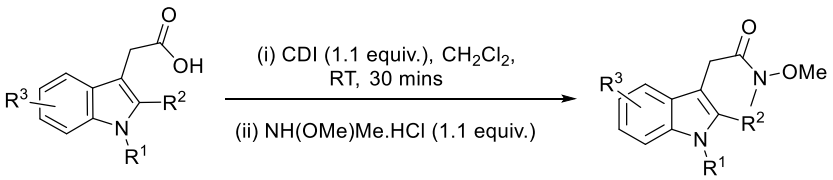
SM4 [6]



SM5 [7]

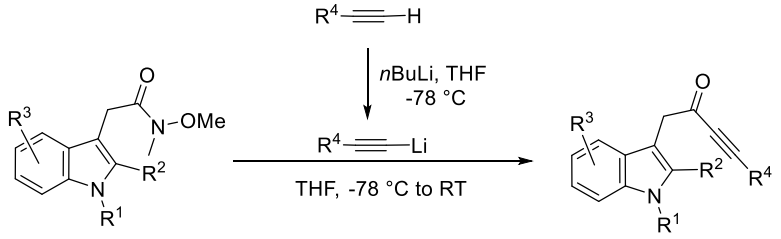
General Information

General Procedure A: Weinreb Amide Synthesis [1]



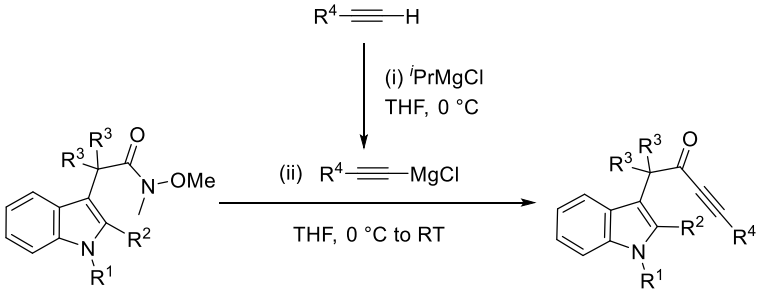
To a suspension of carboxylic acid (1.00 mmol) in CH_2Cl_2 (3 mL) at room temperature (RT) was added CDI (178 mg, 1.10 mmol). A homogeneous solution quickly formed, and was stirred at RT for 30 mins, after which time MeNH(OMe)·HCl (107 mg, 1.10 mmol) was added and stirred for a further 2 h. The crude reaction mixture was then poured into water (10 mL) and basified to pH 10 with 2 M aq. NaOH, extracted with EtOAc (3 × 30 mL) and washed with 10% aq. HCl (15 mL). The organic extracts were then dried over anhydrous $MgSO_4$ and concentrated *in vacuo,* affording the Weinreb amide product which was used without further purification.

General Procedure B: Ynone Formation [1]



To a stirred solution of alkyne (3.00 mmol) in THF (3 mL) at −78 °C under argon was added *n*-BuLi (1.00 mL, 2.5 mmol, 2.5 M in hexanes) dropwise. The mixture was stirred for 30 mins at −78 °C and then transferred via cannula to a −78 °C solution of Weinreb amide (1.00 mmol) in THF (10 mL). Upon complete transfer the mixture was warmed to RT and stirred for 1 h. The reaction was quenched with sat. aq. NH_4Cl (20 mL), diluted with water (30 mL) and extracted with EtOAc (3 × 50 mL). The organic layers were combined, washed with brine (50 mL), dried over Mg_2SO_4, concentrated *in vacuo* and purified by flash column chromatography.

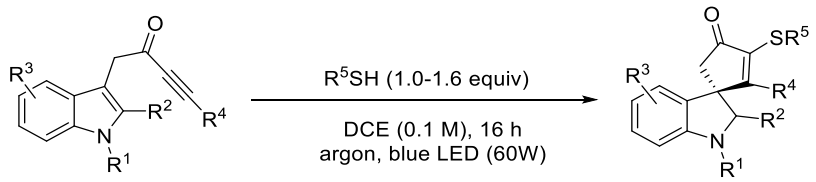
General Procedure C: Ynone Formation



To a stirred solution of alkyne (2.10 mmol, 2.1 equiv) in THF (2 mL) at 0 °C under argon was added *i*PrMgCl (2.00 mmol, 2.0 M in THF) dropwise. The mixture was stirred for 30 mins at 0 °C and was added dropwise to a solution of Weinreb amide (1.0 mmol) in THF (3.3 mL) over 30 mins. The ice bath was removed, and reaction was further stirred at RT for 3 h. The reaction was quenched with sat. aq. NH_4Cl (10 mL), diluted with water (10 mL) and extracted with EtOAc (3 × 10 mL). The organic layers

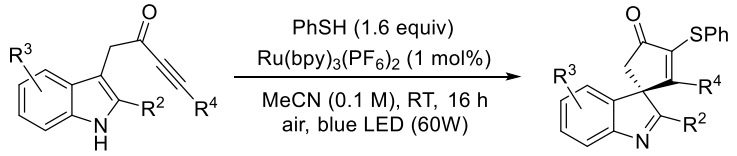
were combined, washed with brine (20 mL), dried over Mg_2SO_4, concentrated *in vacuo* and purified by flash column chromatography.

General procedure D: Thiol-spirocyclisation



To a 8.0 mL screw-neck-vial (17 x 60 mm) equipped with a septa seal screw cap and stirrer bar was loaded thiol (0.20–0.32 mmol, 1.0–1.6 equiv) and ynone (0.2 mmol) in degassed DCE (2 mL, 0.1 M). The mixture was sparged with argon while stirring for 5 mins. After completion of sparging, the vial was additionally sealed with paraffin film and stirred for 16 h under irradiation of a 60 W blue LED flood light (1–2 cm away). A cooling fan was mounted on top of the photoreactor box to maintain ambient reaction temperature (25–30 °C). After completion of the reaction, the solution was concentrated *in vacuo* and purified by flash column chromatography. See next page (S6) for photographs illustrating the argon sparge and reaction set-up.

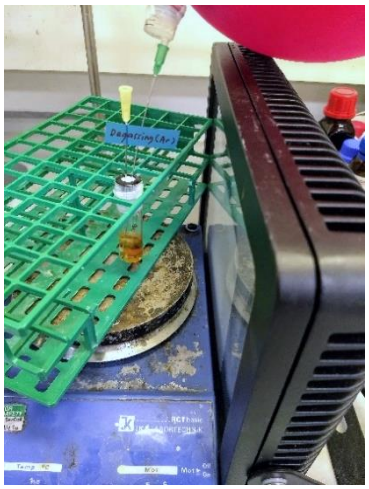
General procedure E: Photoredox conditions



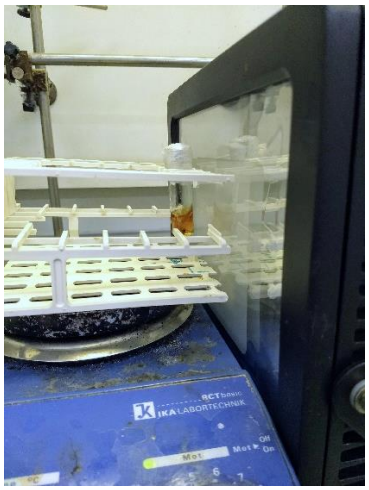
Thiophenol (0.32 mmol, 1.6 equiv) was added to the solution of the indolyl-ynone **13** (0.2 mmol) and $Ru(bpy)_3(PF)_2$ (1mol%) in MeCN (0.1 M). The reaction mixture was sealed under air and stirred for 16 h under the irradiation of 60W blue LED flood light (1–2 cm away) with a cooling fan. After completion of the reaction, the solution was concentrated *in vacuo* and purified by flash column chromatography. See next page (S6) for photographs illustrating the reaction set-up.

General procedure: Images of photochemistry experimental set up

1. Sparging of reaction mixture with argon balloon




2. Sealed reaction vial ready to run

3. Reaction in progress covered in a black box with a cooling fan.

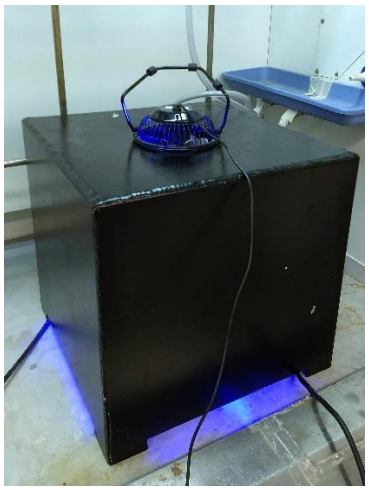
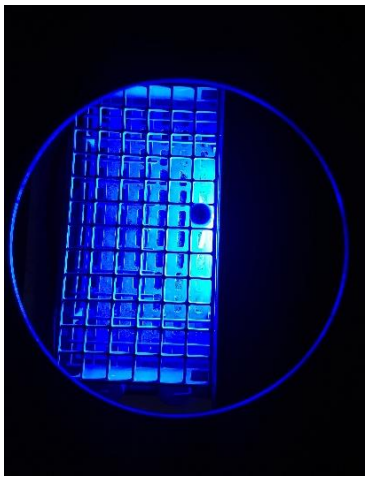
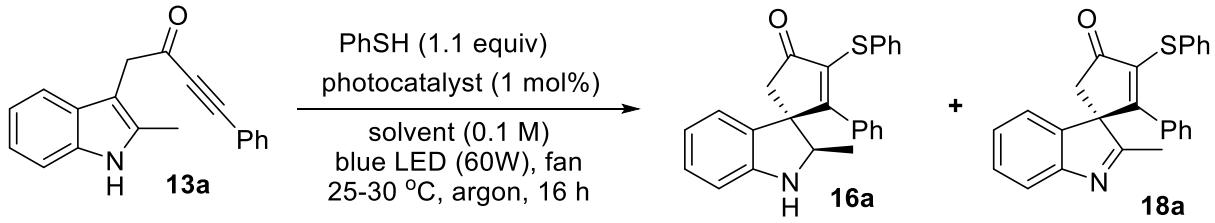



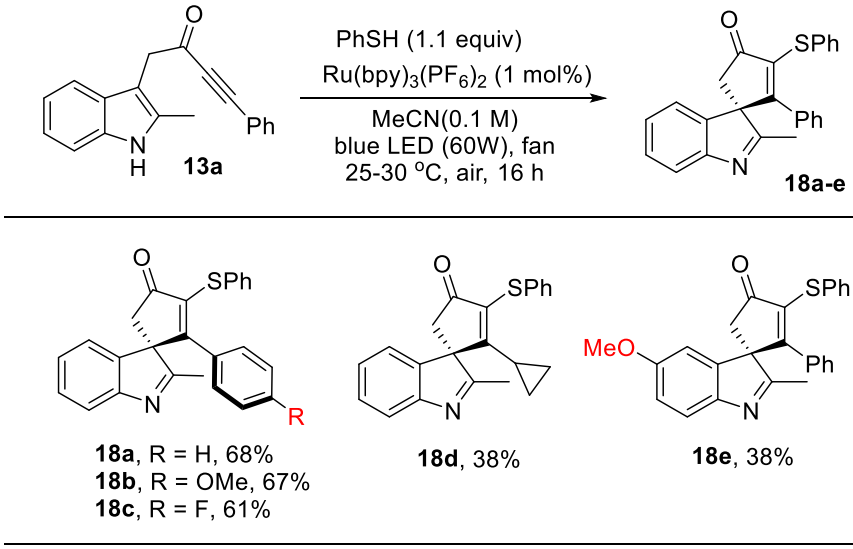
Table S1. Optimisation with thiophenol (PhSH).



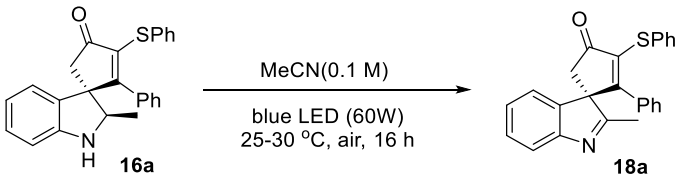
entry	photocatalyst (1 mol%)	solvent (0.1M)	yield of **16a** (%)[a]	yield of **18a** (%)[a]
1	$Ru(bpy)_3(PF_6)_2$	MeCN	(63)	(17)
2[b]	$Ru(bpy)_3(PF_6)_2$	MeCN	(8)	(68)
3[b, c]	$Ru(bpy)_3(PF_6)_2$	MeCN	4	42
4[d]	$Ru(bpy)_3(PF_6)_2$	MeCN	0	0
5	-	MeCN	(60)	(9)
6	-	MeOH	48	52
7	-	DMF	0	0
8	-	DMSO	0	0
9	-	DCE	(66)	(10)
10[d]	-	DCE	0	0
11[e]	-	DCE	10	55
12[b, f]	-	DCE	6	54
13[g]	-	DCE	(84)	Trace
14[g]	-	DCE (0.01M)	48	42

Reaction conditions: **13a** (0.10 mmol), PhSH (0.11 mmol), photocatalyst (1.0 mol%), degassed solvent (0.1 M), stirred under argon atmosphere with irradiation of blue LED light for 16 h. [a] ^1H NMR yield determined by using CH_2Br_2 or 1,3,5-trimethoxybenzene as internal standard. Isolated yields are shown in parentheses. [b] Sealed in air condition. [c] Reaction under CFL bulb (23W). [d] Reaction in the dark. [e] Reaction sealed under oxygen atmosphere. [f] with additional 5 mol% of PhSSPh. [g] Reaction with 1.6 equivalent of PhSH.

Scheme S1. Substrate scope of photoredox-catalysed radical spirocyclisation.



Scheme S2. Visible light-mediated oxidation of **16a** to **18a** under air



entry	variation from above condition	yield of **18a** (%)
1	-	(92)
2	reaction in dark	0
3	reaction under Argon	10

^{1}H NMR yield determined by using CH_2Br_2 as internal standard. Isolated yield shown in parenthesis

Table S2

Quantum Yield Measurements

Quantum yield of the reaction was measured based on reported methods by Yoon *et al* [8a] and the calculations at λ = 455 nm (Φ = 0.85) by Xia *et al.*[8b]

The photon flux of the LED set up was measured by standard ferrioxalate actinometry.[9] Cuvettes were placed 1 cm from the LED light source.

Sample calculations:

Mol of Fe^{2+} = $\frac{v.\Delta A}{l.\varepsilon} = \frac{0.025 \cdot 0.99463}{1 \cdot 11100} = 2.24 \times 10^{-7}\ mol$

Photon flux, = $\frac{mol\ Fe^{2+}}{\Phi \cdot t \cdot f} = \frac{2.24 \times 10^{-7}}{0.85 \cdot 30 \cdot 0.99463} = 8.83 \times 10^{-9}$ einstein s^{-1}

Average photon flux from three experiments = 8.58×10^{-9} einstein s^{-1}.

Thiophenol **11a** (35 µL, 0.32mmol), **13k** (54.6 mg, 0.2 mmol) and DCE (2.0 mL) were charged into a glass cuvette equipped with a PTFE septum and a magnetic stirrer bar. The mixture was further sparged with argon while stirring for 5 mins. After sparging was complete, additional parafilm was sealed on top of the cuvette and the reaction was irradiated with a 60 W blue LED (1 cm away) for 15 min with stirring and cooling from a small fan to maintain ambient temperature.

^{1}H NMR yield = 64%

Sample calculation:

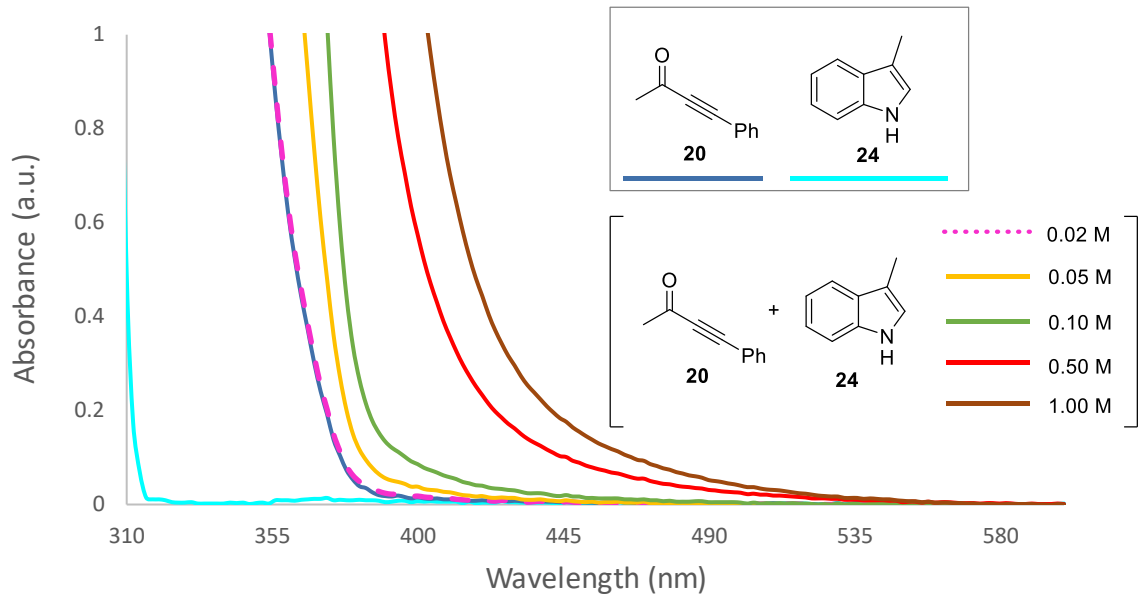
Quantum yield, $\Phi = \frac{mol\ of\ product}{photon\ flux \cdot t \cdot f} = \frac{1.28 \times 10^{-4}}{8.83 \times 10^{-9} \cdot 900 \cdot 0.8408} = 19.2$

Average quantum yield from three experiment: 19.8

UV-Vis Spectroscopy Studies

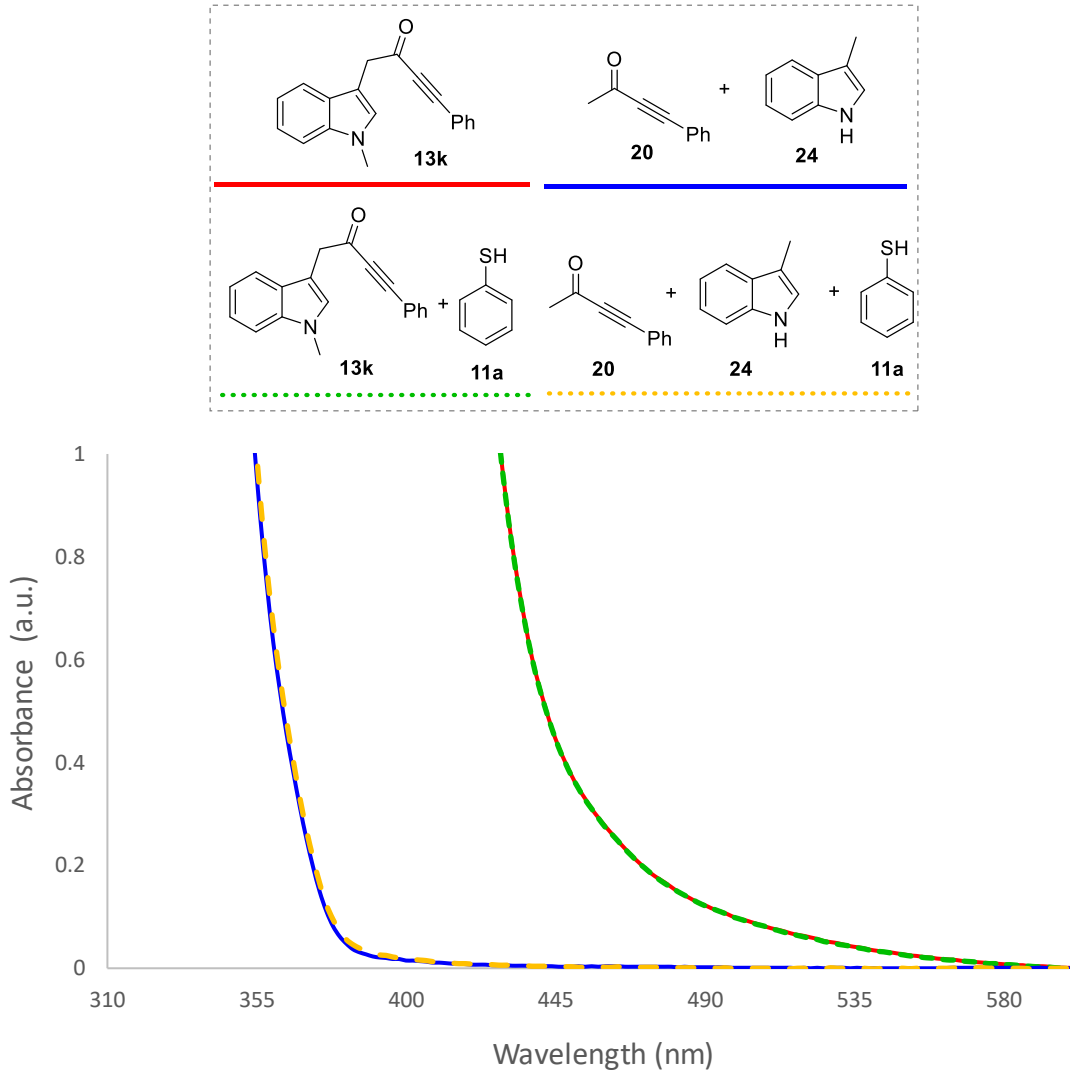
UV-vis spectra were recorded using Shimadzu UV-Vis Spectrophotometer UV-2600 system. A quartz cuvette with 10mm path length (Hellma Macro, AS4C-QS/QG,) was used. Substrates were dissolved in anhydrous 1,2-dichloroethane (0.02 M) unless otherwise stated.

Equimolar quantities of skatole (**24**) and ynone (**11a**) in 1,2-dichloroethane with different concentrations (0.02 M, 0.05 M, 0.10 M, 0.50 M, 1.00 M) were analysed between 300–600nm. Bathochromic shifts were observed with increasing concentration of reaction components support the formation of intermolecular EDA complex.



Scheme S3. UV-vis spectroscopy studies of ynone **20**, indole **24,** and equimolar mixture **20** and **24** in different concentration.

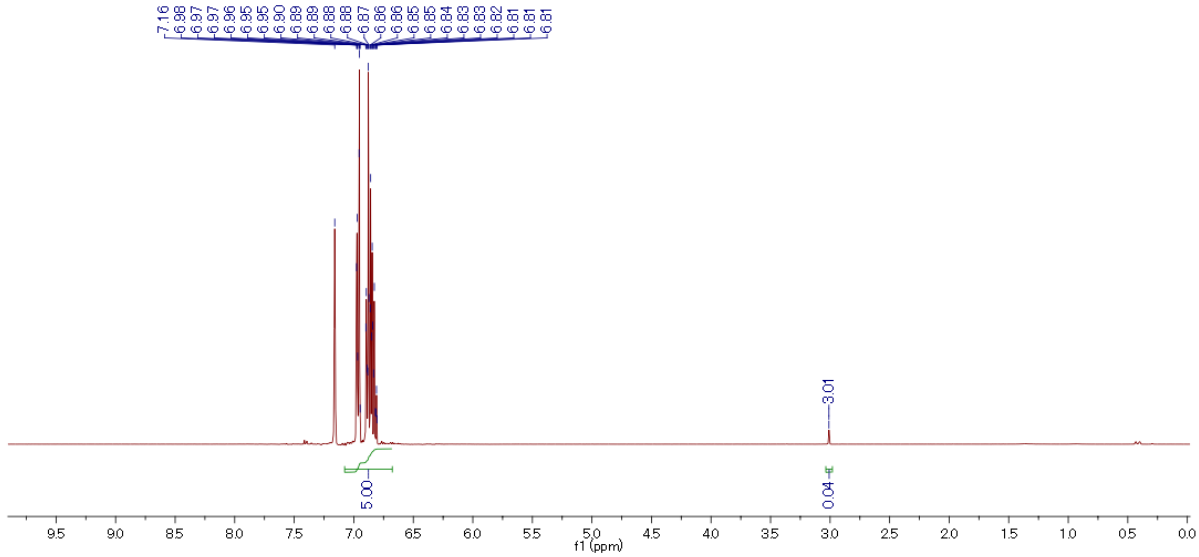
In addition, no red-shift was observed with additional 1 equivalent of thiophenol **11a** solution of **13K** (0.02M in 1,2-dichloroethane), as shown in Scheme S4.



Scheme S4. UV-vis spectroscopy studies of indolyl-ynone **13K** and model reaction components (0.02M in 1,2-dichloroethane).

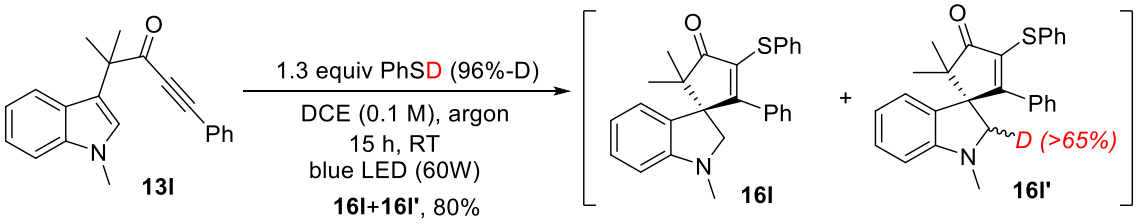
Deuteration studies

Preparation of PhSD: PhSD was synthesised according to reported literature procedure.[13] PhSD with 96% D-incorporation was obatined.

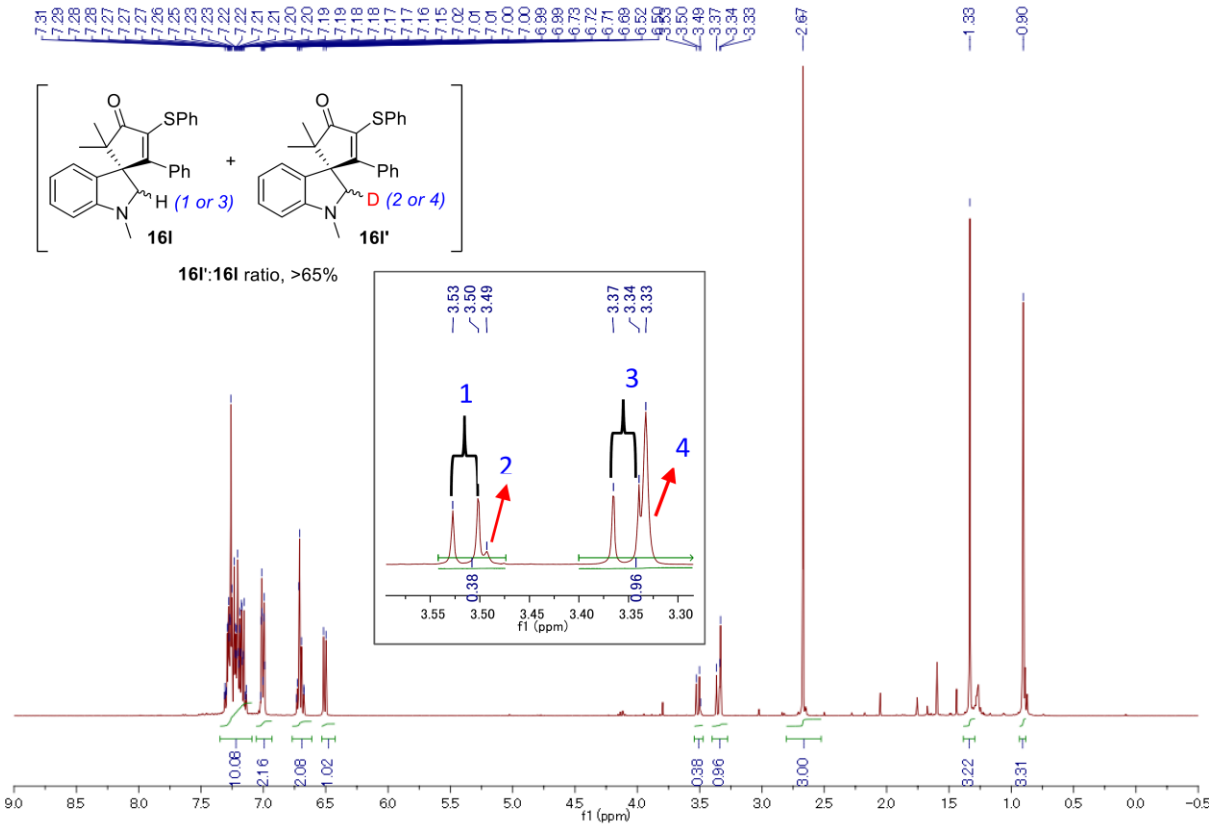


Scheme S5

This freshly prepared sample of PhSD was then reacted with ynone **13l** under the standard conditions (General procedure D) and the product was formed in good yield with 65% deuteration at the expected indole C2-position. We believe that fast proton exchange (PhSD → PhSH) with adventitious water in the reaction system most likely explains why full deuterium incorporation was not observed.

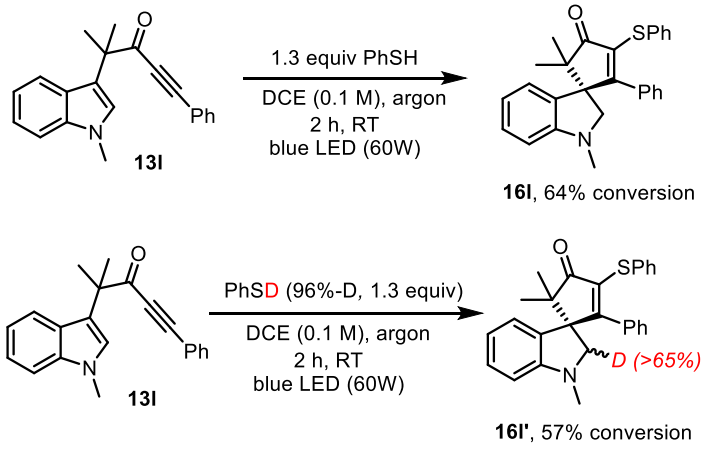


Scheme S6



Scheme S7

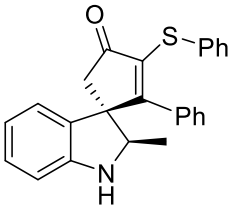
To assess qualitatively whether there is a significant kinetic isotope effect for the HAT step, the rates of the reactions of ynone **13l** with PhSH and PhSD were compared. Both reactions were performed under the standard conditions (general procedure D) but stopped before reaching completion (2 hour reaction time). Based on the percentage conversion to product (assessed using ^{1}H NMR against an internal standard) we can conclude that there is only a small difference in the rates of these reactions, suggesting that the HAT step is not rate determining.

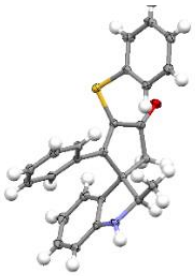


Scheme S8

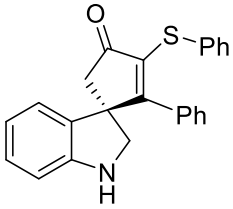
X-Ray Crystallography

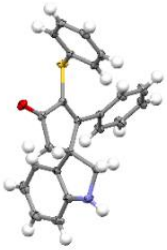
Compounds **13g** (CCDC 1945620), **13k** (CCDC 1945621), **16a** (CCDC 1945619), **16g** (CCDC 1945660), and **16j** (CCDC 1945618), were confirmed by X-ray crystallography. Supplementary crystallography data can be downloaded free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.



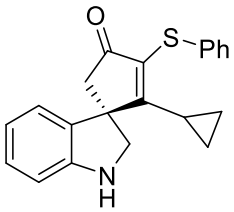


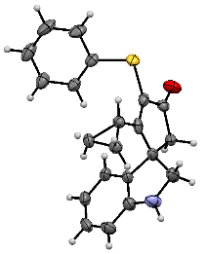
16a, (CCDC 1945619)



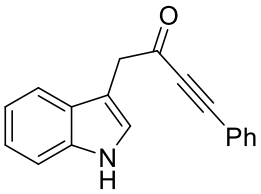


16g, (CCDC 1945660)

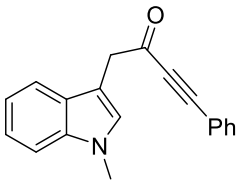


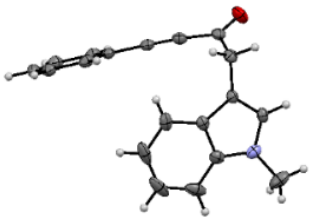


16j, (CCDC 1945618)



13g, (CCDC 1945620)





13k, (CCDC 1945621)

Cyclic Voltammetry

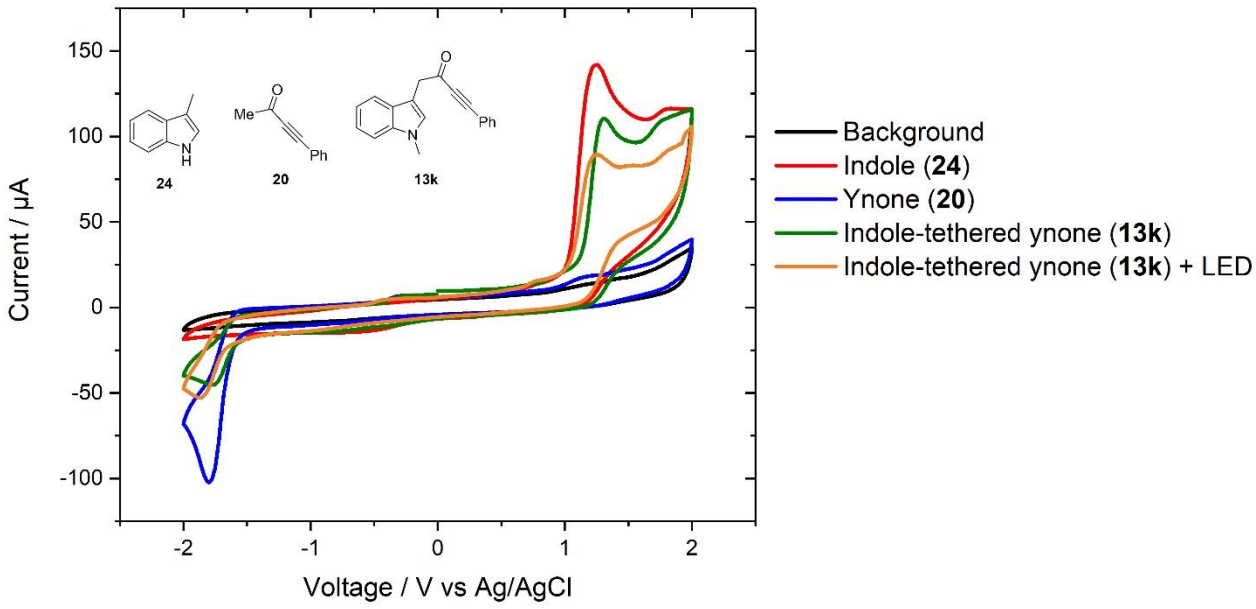


Figure S1. Overlaid cyclic voltammograms of an analyte-free control ("background"), indole **24**, ynone **20** and ynone-tethered ynone **13k** before and during irradiation with blue LED light, as indicated by the legend. All analytes were investigated at a concentration of 4.8 mM in a N_2-saturated solvent of acetonitrile containing Bu_4NPF_6 as electrolyte. The starting potential of 0.0 V vs 3 M KCl Ag/AgCl reference was applied for an equilibration time of 5 sec, the working electrode voltage was then scanned up to a maximum of 2 V and down to a minimum of -2 V at a rate of 100 mV s^{-1} three times and the third voltage sweep is plotted.

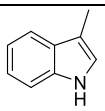
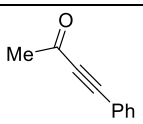
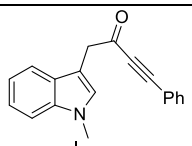
As shown in Figure S1, electrochemical experiments were conducted to determine if the existence of the proposed EDA complex could be detected by comparing the voltammetric response of the indole-tethered ynone moiety (**13k**) to that of the separate indole-only (**24**) and ynone-only (**20**) fragments. The cyclic voltammograms were performed using a 5 mL electrochemical cell vial containing a glassy carbon disk working electrode, platinum counter electrode and Ag/AgCl reference electrode, all from the IKA ElectraSyn range. The cell lid was modified in-house to permit connection to an EmStat potentiostat and the data was collected using the complementary PSTrace software.

The same procedure was followed for experiments conducted on all three analytes and the irradiated sample. First, 77 mg of tetrabutylammonium hexafluorophosphate (0.2 mmol Bu_4NPF_6, Acros Organics, 98%) was added to the cell vial, the lid was attached and then the vial was purged with N_2 for approximately 5 min via the access port. After this, 2 mL dried acetonitrile was added then three control "background" cyclic voltammograms were recorded over a range of -2 V to +2 V at a scan rate of 100 mV s^{-1} and under an atmosphere of N_2 (achieved by attaching a N_2-filled balloon to the cell lid). A 0.1 mL aliquot of 0.1 M analyte in acetonitrile was then added to the cell (final concentration 4.8 mM) and three cyclic voltammograms were recorded under the same conditions. For the irradiated sample, the vial was exposed to a 455 nm blue LED during the cyclic voltammogram. The current was observed to steadily drop during the experiments on each analyte, reflecting that the surface area of the working electrode was being coated by non-conductive material(s). Therefore, in all cases voltammetric data from the third potential sweep is shown in the Figure and between experiments the electrode surface was cleaned by abrasion using alumina.

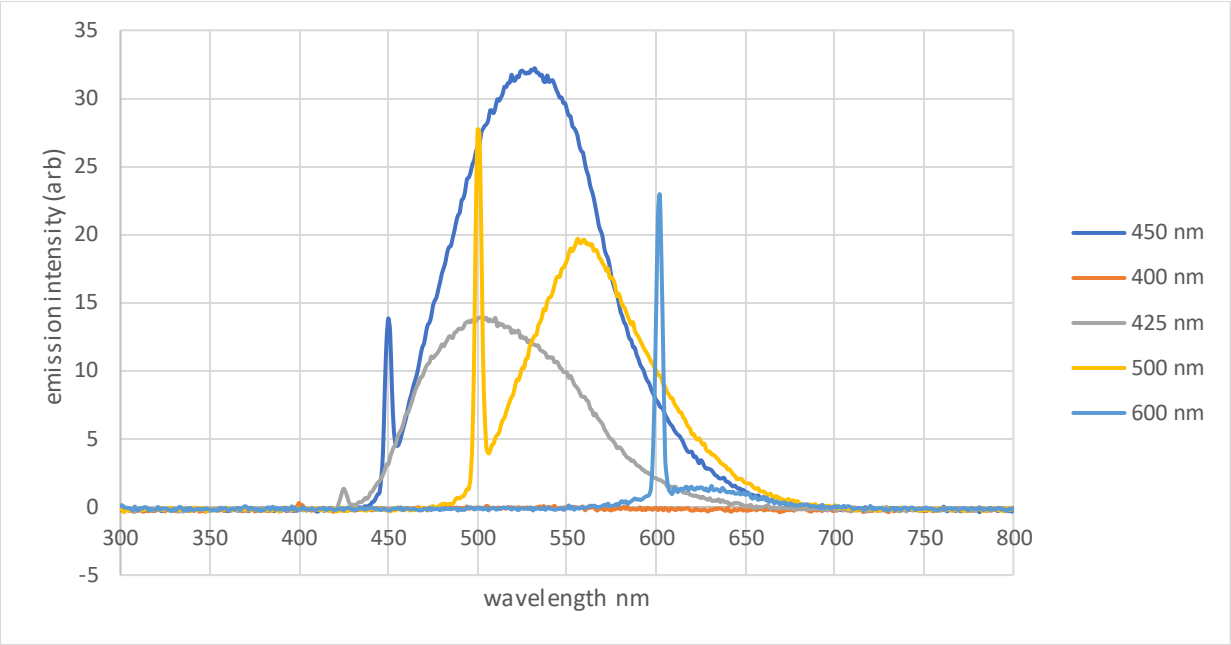
Because of the working electrode passivation and subsequent abrasive surface cleaning it is not possible to attribute any significance to the difference in peak current values between experiments. Instead, it is the position of the current-signals on the voltage axis which is compared, as summarised in Table S3. The peak in positive current indicates that the indole component is susceptible to the same irreversible oxidation process in both the indole-tethered ynone moiety and the indole-only fragment. Conversely, the peak in negative current is correlated to irreversible reduction of the ynone. There are no significant differences observed between the redox reactivities of the indole-tethered ynone and the separate fragments to support EDA complex formation.

Cyclic voltammetry of the indole-tethered ynone was also measured under photo-irradiation conditions in case the formation of the photo-excited state could be detected via changes in the redox properties of the molecule. The fact that no significant changes can be seen in the voltammetry is inconclusive; it may mean that either the efficiency of photo-excitation is too low to generate a detectable concentration of the photo-excited state, or the photo-excited state might not possess measurably changed redox properties. Furthermore, for the proposed initiation mechanism to be valid, only a small percentage of ynone is needed to form an EDA complex and undergo photoexcitation.

Table S3. Summary of the voltage axis position of the maxima in oxidative (positive) current, E_{ox}, and reductive (negative) current, E_{red} from the data in Figure S1.

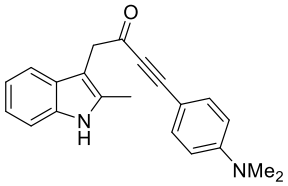
				
	Indole	**Ynone**	**Indole-tethered ynone**	**Indole-tethered ynone + LED**
E_{ox} / V vs Ag/AgCl	+1.24	-	+1.25	+1.24
E_{red} / V vs Ag/AgCl	-	-1.80	-1.76	-1.87

Emission spectra for 13g (0.02M in DCE)



Characterisation data and synthetic procedures

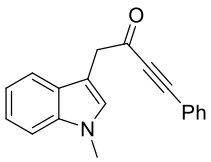
4-(4-(Dimethylamino)phenyl)-1-(2-methyl-1H-indol-3-yl)but-3-yn-2-one, 13d



Synthesised using general procedure **B** with 4-ethynyl-*N,N*-dimethylaniline (871.0 mg, 6.0 mmol), *n*-BuLi (2.0 mL, 5 mmol, 2.5 M solution in hexane), THF (6 mL), *N*-methoxy-*N*-methyl-2-(2-methyl-1H-indol-3-yl)acetamide[2] (464.6 mg, 2.0 mmol in 20 mL THF). Purification by flash column chromatography (hexane:EtOAc, 7:3 *v/v*) afforded the *title product* **13d** (299.0 mg, 47%) as yellow solid. Mp: 88–90°C; R_f = 0.34 (hexane:EtOAc, 7:3 *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.62–7.60 (m, 1H), 7.30–7.28 (m, 1H), 7.18 (d, *J* = 8.8 Hz, 2H), 7.14-7.12 (m, 2H), 6.53 (d, *J* = 8.8 Hz, 2H), 3.96 (s, 2H), 2.99 (s, 6H), 2.44 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 185.6, 151.7, 135.4, 135.2, 133.4, 129.0, 121.3, 119.7, 118.4, 111.5, 110.4, 105.7, 104.5, 96.2, 88.9, 41.1, 40.1, 12.0; **HRMS** (ESI$^+$) calcd for $C_{21}H_{20}N_2NaO$ [MNa]$^+$: 339.1468, found: 339.1468 (0.1 ppm error); ν_{max} (thin film)/cm^{-1}: 3399, 2186, 2150, 1646, 1596, 1525.

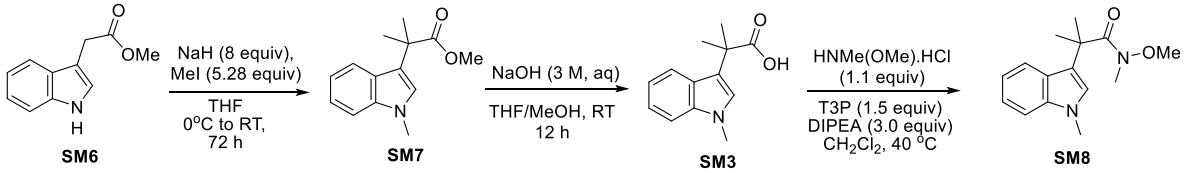
1-(1-Methyl-1H-indol-3-yl)-4-phenylbut-3-yn-2-one, 13k



Synthesised using general procedure **C** with phenylacetylene (3.29 mL, 30 mmol), *i*PrMgCl (14.25 mL, 28.5 mmol, 2.0 M solution in hexane), THF (30 mL), Weinreb amide **SM2** (3.48 g, 15.0 mmol in 50.0 mL THF). Purification by flash column chromatography (hexane:EtOAc 4:1, *v/v*) afforded the *title* **13k** (3.48 g, 85%) as yellow solid. Mp: 62–63 °C; R_f = 0.54 (hexane:EtOAc, 7:3 *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 1H), 7.31–7.26 (m, 2H), 7.22–7.12 (m, 4H), 7.05 (t, *J* = 7.1 Hz, 1H), 6.95 (s, 1H), 3.97 (s, 2H), 3.64 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 185.6, 137.1, 133.1, 130.7, 128.6, 128.4, 128.0, 121.9, 120.0, 119.4, 119.1, 109.5, 105.9, 91.9, 88.2, 42.0, 32.8; **HRMS (ESI)** calcd for $C_{19}H_{15}NNaO$ [MNa]$^+$: 296.1046, found: 296.1043 (0.8 ppm error); ν_{max} (thin film)/cm^{-1}: 2201, 1662, 1670, 740.

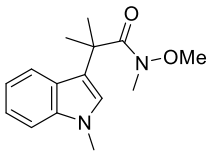
Preparation of SM8 from methyl 2-(1H-indol-3-yl)acetate (SM6)



SM3 was prepared by modified literature procedure from commercially available **SM6**. [3] To a dried 250 mL round-bottom flask with a stirrer bar was loaded NaH (8.64 g, 216 mmol, 8 equiv.) and rinsed with hexane (20 mL) under an argon atmosphere and followed by anhydrous THF (50 mL). While stirring, **SM6** (5.44 g, 28.7 mmol, 1 equiv) in THF (50 mL) was added slowly at 0 °C and ice bath was removed and further stirred at RT for 0.5 h. Iodomethane (8.88 mL, 142.6 mmol, 5.28 equiv) dissolved in THF (50 mL) was added to the mixture at 0 °C and allowed to stir at RT for 72 h. The reaction was carefully quenched with MeOH (5 mL) and sat. NH_4Cl (aq) solution (5 mL) at 0 °C, further extracted with diethyl ether (3 x 100 mL). The organic layers were combined and washed with sat. brine solution and dried with anhydrous Na_2SO_4. The organic solvent was then removed *in vacuo*. Purification by column chromatography (hexane:EtOAc, 5:1 *v/v*) afforded **SM7** (1.33 g, 20%) as beige solid. **SM7** (1.33 g, 5.75 mmo) was then hydrolysed by stirring with NaOH (2.0 mL, 3N aq.) in THF/MeOH (1:1, 5.5 mL) at 50 °C for 12 h, after which the mixture was acidified to pH 3–4 using 2.0 N aq. HCl and excess solvent

was removed *in vacuo.* Water (10 mL) was added to the reaction mixture and it was then extracted with EtOAc (3 x 20 mL). The organic layers were combined and washed with sat. brine solution (aq) and dried with anhydrous Na_2SO_4. Upon removal of solvent afforded **SM3** (1.00 g, 4.6 mmol) which was used directly without purification.

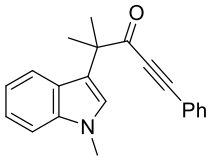
***N*-Methoxy-N,2-dimethyl-2-(1-methyl-1H-indol-3-yl)propenamide, SM8**



SM8 was prepared by using with **SM3** (223.7 mg, 1.0 mmol), T3P® (0.97 mL, 1.5 mmol), CH_2Cl_2 (2.5 mL), DIPEA (0.53 mL, 3.0 mmol) and MeNH(OMe)·HCl (109.0 mg, 1.1 mmol) stirred at 40 °C for 15 h. Purification by column chromatography afford *title compound* **SM8** (220.0 mg, 85%) as beige solid. Mp: 92–94 °C; R_f = 0.50 (hexane:EtOAc, 2:1 *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.4 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.20 (*app* t, *J* = 8.4 Hz, 1H), 7.08–7.04 (m, 1H), 3.79 (s, 3H), 3.08 (s, 3H), 2.65 (s, 3H), 1.66 (s, 6H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 177.1, 137.0, 126.3, 124.3, 121.5, 120.4, 120.2, 119.0, 109.2, 59.4, 41.8, 33.7, 32.7, 26.4; **HRMS** (ESI$^+$) calcd for $C_{15}H_{21}N_2O_2$ [MH]$^+$:261.1588, found: 261.1598 (3.7 ppm error); ν_{max} (thin film)/cm^{-1}: 1646, 741.

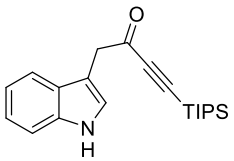
4-Methyl-4-(1-methyl-1H-indol-3-yl)-1-phenylpent-1-yn-3-one, 13l



Prepared by using general **procedure D** using phenylacetylene (182.0 µL, 1.66 mmol), *i*PrMgCl (0.83 mL, 1.66 mmol, 2.0 M solution in THF), THF (2.0 mL) at 0 °C for 0.5 h. **SM8** (216 mg, 0.83 mmol) dissolved in THF (3.0 mL) was added dropwise at 0 °C, and stirred at RT for 12 h. Purification by column chromatography (hexane: DCM, 4:1 → 2:1 *v/v*) afforded the *title compound* **13l** as pale yellow solid. Mp: 121–123 °C, R_f = 0.24 (hexane:CH_2Cl_2 = 2:1 *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz, 1H), 7.38–7.20 (m, 3H), 7.11-7.07 (m, 1H), 7.03 (s, 1H), 3.80 (s, 3H), 1.75 (s, 6H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 191.3, 158.2, 137.6, 132.9, 130.2, 128.4, 126.4, 121.6, 120.6, 120.4, 119.2, 117.3, 109.4, 92.0, 86.8, 48.4, 32.9, 24.8; **HRMS** (ESI$^+$) calcd for $C_{21}H_{20}NO$ [MH]$^+$: 302.1539, found: 302.1539 (0.2 ppm); ν_{max} (thin film)/cm^{-1}: 2198, 1660, 1063, 740, 689

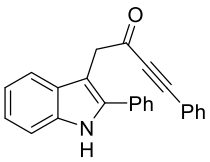
1-(1H-Indol-3-yl)-4-(triisopropylsilyl)but-3-yn-2-one, 13o



Synthesised using **general procedure B** with ethynyltriisopropylsilane (2.73 g, 15.0 mmol), *n*BuLi (5.0 mL, 12.5 mmol), THF (15 mL) and *N*-methoxy-*N*-methyl-2-(2-phenyl-1H-indol-3-yl)acetamide (1.09 g, 5.00 mmol dissolved in 100 mL THF). Purificatoin using silica gel chromatography (hexane:EtOAc, 4:1 *v/v*) afforded to *title compound* **13o** (1.27 g, 75%) as yellow oil; R_f = 0.42 (hexane EtOAc, 4:1 *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (br s, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.22–7.11 (m ,3H), 3.99 (s, 2H), 1.02–0.99 (m, 21H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 185.4, 136.1, 127.4, 123.6, 122.3, 119.8, 118.8, 111.1, 107.6, 104.0, 96.9, 42.0, 18.3, 10.8; **HRMS** (ESI$^+$) calcd for $C_{21}H_{30}NNaOSi$ [MH]$^+$: 362.1914, found: 362.1911 (-0.3 ppm error); ν_{max} (thin film)/cm^{-1}: 2943, 2865, 2147, 1664, 1548, 1095, 738.

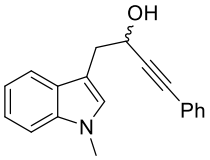
4-Phenyl-1-(2-phenyl-1H-indol-3-yl)but-3-yn-2-one, 13r



Synthesised using **general procedure B** with phenylacetylene (0.72 mL, 6.47 mmol), *n*BuLi (2.16 mL, 5.4 mmol), THF (6.5 mL) and **SM10** (635 mg, 2.16 mmol dissolved in 70 mL THF). Purification using silica gel chromatography (hexane:EtOAc , 4:1 *v/v*) afforded to *title compound* **13r** (145 mg, 20%) as pale yellow oil; R_f = 0.35 (hexane EtOAc, 3:1 *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (br s, 1H), 7.58 (d, J = 7.9 Hz, 1H), 7.63–7.60 (m, 2H), 7.49–7.45 (m, 2H), 7.41–7.37 (m, 3H), 7.29–7.15 (m, 6H), 4.15 (s, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 185.9, 136.7, 135.8, 133.1, 132.3, 130.7, 129.2, 129.0, 128.4, 128.2, 128.1, 122.7, 120.2, 119.8, 119.4, 110.9, 104.7, 92.3, 88.3, 41.7; **HRMS** (ESI$^+$) calcd for $C_{24}H_{18}NO$ [MH]$^+$: 336.1384, found: 336.1383 (-1.1 ppm error); ν_{max} (thin film)/cm^{-1}: 3380, 2201, 1655, 1489, 757, 741.

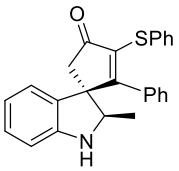
1-(1-Methyl-1H-indol-3-yl)-4-phenylbut-3-yn-2-ol, 13n



Prepared according to a literature report. [10] In a round bottom flask with a stirrer bar was charged with **13k** (300 mg, 1.09 mmol) and MeOH (22.0 mL, 0.05 M). $NaBH_4$ (166.3 mg, 4.4 mmol, 4 equiv) was added portion wise at 0 °C and the mixture was stirred at RT for 1 h. After completion of reaction, reaction was cooled to 0 °C followed by slow addition of 5 mL of sat. NH_4Cl (aq) solution. The reaction mixture was extracted with CH_2Cl_2 (3 x 10 mL), washed with saturated brine solution and dried with anhydrous Na_2SO_4. The solvent was then removed *in vacuo*, and the product purified by column chromatography (hexane:EtOAc, 3:1 *v/v*) affording the *title compound* **13n** as a pale-yellow oil (280.0 mg, 99%). R_f = 0.42 (hexane:EtOAc = 3:1 *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.8 Hz, 1H), 7.40–7.37 (m, 2H), 7.34–7.23 (m, 5H), 7.15–7.12 (1H), 7.06 (s, 1H), 4.87 (dd, *J* =7.0, 5.6 Hz, 1H), 3.79 (s, 3H), 3.33 (dd, *J* = 14.7, 5.6 Hz, 1H), 3.25 (dd, *J* = 14.7, 7.0 Hz, 1H), 2.11 (s broad, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 137.0, 131.7, 128.3, 128.2, 128.2, 122.7, 121.8, 119.3, 119.1, 109.3, 108.9, 90.1, 84.9, 63.0, 33.9, 32.7;**HRMS** (ESI$^+$) calcd for $C_{19}H_{18}NO$ [MH]$^+$: 276.1383, found: 276.1379 (1.4 ppm error); ν_{max} (thin film)/cm^{-1}: 2913, 1488, 1473, 1029, 1011, 756, 736, 690.

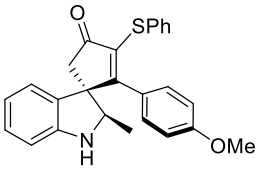
2'-Methyl-2-phenyl-3-(phenylthio)spiro[cyclopentane-1,3'-indolin]-2-en-4-one, 16a



Synthesised using **general procedure D** with thiophenol (32 µL, 0.32 mmol), ynone **13a** (54.6 mg, 0.2 mmol) and DCE (2 mL). Purification by column chromatography (hexane:EtOAc, 7:3 *v/v*) afforded the *title compound* **16a** (58 mg, 76%) as a yellow solid. Mp: 155–157 °C; R_f = 0.32 (hexane:EtOAc, 7:3 *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.21 (m, 11H), 6.92 (t, *J* = 7.7 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 2H), 4.06 (q, *J* = 6.5 Hz, 1H), 3.78 (br, 1H), 3.24 (d, *J* = 19.0 Hz, 1H), 2.67 (d, *J* = 19.0 Hz, 1H), 1.23 (d, *J* = 6.5 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 202.6, 177.0, 151.6, 135.9, 135.3, 133.8, 131.2, 129.4, 129.2, 129.1, 128.8, 127.9, 127.6, 126.4, 123.4, 120.1, 110.6, 66.0, 58.5, 48.6, 14.2; **HRMS** (ESI$^+$) calcd for $C_{25}H_{22}NOS$ [MH]$^+$: 384.1417, found: 384.1411 (1.6 ppm); ν_{max} (thin film)/cm^{-1}: 1711, 1605, 1480, 1439, 744, 698.

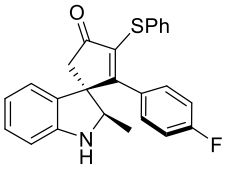
2-(4-Methoxyphenyl)-2'-methyl-3-(phenylthio)spiro[cyclopentane-1,3'-indolin]-2-en-4-one, 16b



Synthesised using **general procedure D** with thiophenol (32 µL, 0.32 mmol), ynone **16b** (60.6 mg, 0.2 mmol) and DCE (2 mL). Purification by column chromatography (hexane:EtOAc ,10:1 → 5:1 *v/v*) afforded the *title compound* **16b** (45 mg, 55%) as a yellow solid. Mp: 59–61 °C; R_f = 0.29 (hexane:EtOAc, 4:1 *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.12 (m, 7H), 6.91 (t, *J* = 7.7 Hz, 1H), 6.70–6.65 (m, 5H), 4.09 (q, *J* = 6.7 Hz, 1H), 3.74 (s, 3H), 3.25 (d, *J* = 18.9 Hz, 1H), 2.67 (d, *J* = 19.0 Hz, 1H), 1.22 (d, *J* = 6.8 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 202.7, 177.0, 160.3, 151.6, 134.6, 134.1, 131.5, 129.7, 129.3, 128.8, 127.5, 126.3, 123.5, 120.1, 113.0, 110.5, 66.1, 58.4, 55.0, 49.4, 14.4; **HRMS** (ESI$^+$) calcd for $C_{26}H_{24}NO_2S$ [MH]$^+$: 141.1522, found: 414.1526 (–1.0 ppm); $\mathbf{\nu_{max}}$ (thin film)/cm^{-1} : 1707, 1604, 1504, 1250, 1179, 738.

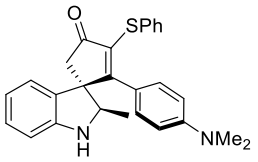
2-(4-Fluorophenyl)-2'-methyl-3-(phenylthio)spiro[cyclopentane-1,3'-indolin]-2-en-4-one, 16c



Synthesised using **general procedure D** with thiophenol (32 µL, 0.32 mmol), ynone **13c** (58.2 mg, 0.2 mmol) and DCE (2.0 mL). Purification by column chromatography (hexane:EtOAc, 7:3 *v/v*) afforded the *title compound* **16c** (55 mg, 68%) as a yellow solid. Mp: 57–59 °C; R_f = 0.35 (hexane:EtOAc, 7:3 *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.12 (m, 7H), 6.91 (td, *J* = 7.4, 0.9 Hz, 1H), 6.85–6.80 (m, 2H), 6.66-6.63 (m, 3H), 4.08 (q, *J* = 6.7 Hz, 1H), 3.25 (d, *J* = 19.1 Hz, 1H), 2.68 (d, *J* = 19.1 Hz, 1H), 1.23 (d, *J* = 6.7 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 202.5, 175.6, 162.9 (d, J^1 = 249.7 Hz), 151.5, 136.2, 133.5, 130.1 (d, J^4 = 3.2 Hz), 130.9, 130.0 (d, J^3 = 8.5 Hz), 129.5, 129.3, 128.9, 126.6, 123.3, 120.1, 114.8 (d, J^2 = 21.9 Hz, 1H), 110.5, 65.9, 58.4, 48.7, 14.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –111.09 to –111.16 (m); **HRMS** (ESI$^+$) calcd for $C_{25}H_{20}NNaOS$ [MNa]$^+$: 424.1142, found: 424.1142 (0.0 ppm); $\mathbf{\nu_{max}}$ (thin film)/cm^{-1}: 1710, 1602, 1502, 1481, 1160, 738.

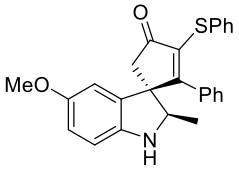
2-(4-(Dimethylamino)phenyl)-2'-methyl-3-(phenylthio)spiro[cyclopentane-1,3'-indolin]-2-en-4-one, 16d



Synthesised using **general procedure D** with thiophenol (32.0 µL, 0.32 mmol), ynone **13d** (63.2 mg, 0.2 mmol) and DCE (2.0 mL). Purification by column chromatography (hexane:EtOAc, 7:3 *v/v*) afforded the *title compound* **16d** (38.0 mg, 45%) as a yellow solid. Mp: 74–76 °C; R_f = 0.24 (hexane:EtOAc, 7:3 *v/v*);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.12 (m, 5H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.74 (d, *J* = 9.0 Hz, 2H), 6.69 (d, *J* = 7.8 Hz, 1H), 6.45 (d, *J* = 9.0 Hz, 2H), 4.11 (q, *J* = 6.6 Hz, 1H), 3.24 (d, *J* = 18.8 Hz, 1H), 2.92 (s, 6H), 2.67 (d, *J* = 18.8 Hz, 1H), 1.20 (d, *J* = 6.6 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 202.8, 178.2, 151.6, 150.9, 135.0, 132.4, 131.9, 130.0, 129.1, 128.8, 128.3, 128.0, 125.9, 123.7, 122.4, 120.1, 110.4, 66.3, 58.3, 50.5, 39.9, 14.6; **HRMS** (ESI$^+$) calcd for $C_{27}H_{27}N_2OS$ [MH]$^+$: 427.1839, found: 427.1840 (-0.3 ppm); $\mathbf{\nu_{max}}$ (thin film)/cm^{-1} : 1702, 1604, 1509, 1482, 1199, 738.

5'-Methoxy-2'-methyl-2-phenyl-3-(phenylthio)spiro[cyclopentane-1,3'-indolin]-2-en-4-one, 16e

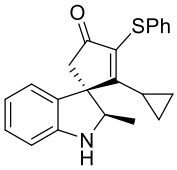


Synthesised using **general procedure D** with thiophenol (32 µL, 0.32 mmol), ynone **16e** (60.6 mg, 0.2 mmol) and DCE (2.0 mL). Purification by column chromatography (hexane:EtOAc, 7:3 *v/v*) afforded the *title compound* **16e** (41.0 mg, 49%) as a yellow solid. Mp:138–140 °C; R_f = 0.28 (hexane:EtOAc, 7:3 *v/v*);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.33 (m, 2H), 7.28–7.23 (m, 6H), 6.88 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.81 (d, *J* = 2.4 Hz, 1H), 6.74 (d, *J* = 8.2 Hz, 2H) 6.70 (d, *J* = 8.2 Hz, 2H), 4.13 (q, *J* = 6.6 Hz, 1H), 3.89 (s, 3H), 3.30 (d, *J* = 19.1 Hz, 1H), 2.76 (d, *J* = 19.1 Hz, 1H), 1.32 (d, *J* = 6.8 Hz, 3H); **^{13}C{^{1}H}**

NMR (100 MHz, $CDCl_3$) δ 202.5, 177.1, 154.6, 145.4, 135.9, 135.2, 133.8, 133.0, 129.3, 129.2, 128.8, 128.0, 127.6, 126.5, 115.0, 112.0, 109.2, 66.4, 59.1, 56.0, 48.3, 14.2.; **HRMS** (ESI^+) calcd for $C_{26}H_{23}NNaO_2S$ $[MNa]^+$: 436.1342, found: 436.1342 (0.0 ppm error); $\mathbf{\nu_{max}}$ (thin film)/cm^{-1} 1712, 1490, 1439, 1223, 738.

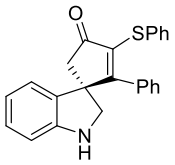
2-Cyclopropyl-2'-methyl-3-(phenylthio)spiro[cyclopentane-1,3'-indolin]-2-en-4-one, 16f



Synthesised using **general procedure D** with thiophenol (32.0 µL, 0.32 mmol), ynone **13f** (47.4 mg, 0.2 mmol) and DCE (2 mL). Purification by column chromatography (hexane:EtOAc, 7:3 *v/v*) afforded the *title compound* **16f** (38.0 mg, 54%) as a yellow solid. Mp: 65–67 °C; R_f = 0.29 (hexane:EtOAc, 7:3 *v/v*);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.32 (m, 2H), 7.26–7.21 (m, 4H), 7.09 (d, *J* = 7.5 Hz, 1H), 6.93 (*app* t, *J* = 7.8 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 4.19 (q, *J* = 6.6 Hz, 1H), 3.15 (d, *J* = 19.1 Hz, 1H), 2.58 (d, *J* = 19.1 Hz, 1H), 1.83-1.67 (m, 3H), 1.49 (d, *J* = 6.5 Hz, 3H), 1.18-1.13 (m, 1H), 0.98-0.94 (m, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 203.0, 189.6, 150.9, 135.7, 132.1, 129.0, 128.9, 127.1, 125.8, 125.8, 123.4, 120.0, 110.2, 65.9, 59.3, 48.7, 15.2, 14.4, 12.9, 12.3; **HRMS** (ESI^+) calcd for $C_{22}H_{21}NNaOS$ $[MNa]^+$: 370.1236, found: 370.1235 (0.2 ppm); $\mathbf{\nu_{max}}$ (thin film)/cm^{-1} 1702, 1568, 1480, 1238, 739.

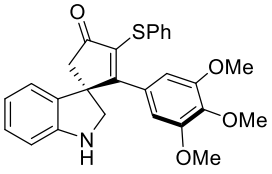
2-Phenyl-3-(phenylthio)spiro[cyclopentane-1,3'-indolin]-2-en-4-one, 16g



Synthesised using **general procedure D** with thiophenol (32.0 µL, 0.32 mmol), ynone **13g** (51.8 mg, 0.2 mmol) and DCE (2 mL). Purification by column chromatography (hexane:EtOAc, *7*:3 *v/v*) afforded the *title compound* **16g** (50.1 mg, 69%) as a yellow solid. Mp: 59–61 °C; R_f = 0.23 (hexane:EtOAc, 7:3 *v/v*);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13–7.02 (m, 10H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.87 (s, 1H), 6.85 (s, 1H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.56 (d, *J* = 7.8 Hz, 1H), 3.69 (d, *J* = 9.8 Hz, 1H), 3.61 (br, 1H), 3.51 (d, *J* = 9.8 Hz, 1H) , 2.96 (d, *J* = 18.8 Hz, 1H), 2.85 (d, *J* = 18.8 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 203.2, 176.8, 151.1, 134.8, 134.0, 133.55, 131.8, 129.8, 129.5, 129.3, 129.0, 128.3, 128.1, 126.8, 122.8, 119.9, 110.5, 57.6, 56.4, 52.4; **HRMS** (ESI^+) calcd for $C_{24}H_{19}NNaOS$ $[MNa]^+$: 392.1080, found: 392.1077 (0.7 ppm); $\mathbf{\nu_{max}}$ (thin film)/cm^{-1} 1710, 1603, 1486, 742, 697.

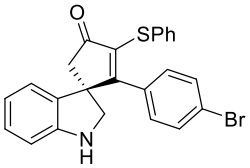
3-(Phenylthio)-2-(3,4,5-trimethoxyphenyl)spiro[cyclopentane-1,3'-indolin]-2-en-4-one, 16h



Synthesised using **general procedure D** with thiophenol (32.0 µL, 0.32 mmol), ynone **13h** (69.8 mg, 0.2 mmol) and DCE (2.0 mL). Purification by column chromatography (hexane:EtOAc, 6:4 → 1:1 *v/v*) afforded the *title compound* **16h** (76.0 mg, 79%) as a yellow solid. Mp: 58–60 °C. R_f = 0.15 (hexane:EtOAc, 6:4 *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.39 (m, 7H), 7.14 (t, *J* = 7.3 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 1H), 6.53 (s, 2H), 4.11 (d, *J* = 9.9 Hz, 1H), 4.10 (s, 3H), 3.94 (d, *J* = 9.9 Hz, 1H), 3.82 (s, 6H), 3.39 (d, *J* = 18.8 Hz, 1H) 3.25 (d, *J* = 18.8 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 203.1, 175.7, 152.4, 151.2, 145.1, 138.7, 133.8, 133.5, 132.1, 129.4, 129.2, 128.8, 126.6, 122.9, 119.6, 110.2, 105.8, 60.8, 57.8, 56.3, 55.6, 52.6; **HRMS** (ESI^+) calcd for $C_{27}H_{26}NO_4S$ $[MH]^+$: 460.1577, found: 460.1578 (–0.2 ppm); $\mathbf{\nu_{max}}$ (thin film)/cm^{-1}: 1709, 1582, 1501, 1488, 1464, 1412, 1337, 1233, 737.

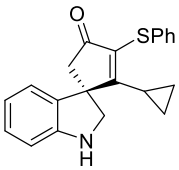
2-(4-bromophenyl)-3-(phenylthio)spiro[cyclopentane-1,3'-indolin]-2-en-4-one, 16i



Synthesised using **general procedure D** with thiophenol (16.0 µL, 0.16 mmol), ynone **13i** (33.7 mg, 0.1 mmol) and DCE (1.0 mL). Purification by column chromatography (hexane:EtOAc, 3:2 *v/v*) afforded the *title compound* **16i** (29 mg, 65%) as a yellow solid. Mp: 139–140 °C; R_f = 0.29 (hexane:EtOAc, 3:2 *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.21-7.13 (m, 6H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.83 (t, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 2H), 6.64 (d, *J* = 7.8 Hz, 1H), 3.73 (d, *J* = 9.9 Hz, 1H), 3.62 (d, *J* = 9.9 Hz, 1H), 3.06 (d, *J* = 18.9 Hz, 1H), 2.91 (d, *J* = 18.9 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 202.8, 174.8, 151.0, 135.2, 132.9, 132.7, 131.2, 131.1, 130.0, 129.7, 129.3, 128.9, 126.9, 123.8, 122.6, 119.8, 110.4, 57.4, 56.1, 51.9; **HRMS** (ESI$^+$) calcd for $C_{24}H_{19}BrNOS$ [MH]$^+$: 448.0365, found: 448.0365 (0.1 ppm); **ν_{max}** (thin film)/cm^{-1}:1712, 1603, 1483, 1009, 742, 697.

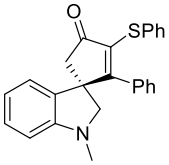
2-Cyclopropyl-3-(phenylthio)spiro[cyclopentane-1,3'-indolin]-2-en-4-one, 16j



Synthesised using **general procedure D** with thiophenol (32.0 µL, 0.32 mmol), ynone **13j** (44.6 mg, 0.2 mmol) and DCE (2.0 mL). Purification by column chromatography (hexane:EtOAc, 3:2 *v/v*) afforded the *title compound* **16j** (67.0 mg, 88%) as a yellow solid. Mp: 62–63 °C; R_f = 0.14 (hexane:EtOAc, 7:3 *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.4 (m, 6H), 7.27 (d, *J* = 7.2 Hz, 1H), 7.11 (t, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 7.8 Hz, 1H), 4.39 (d, *J* = 9.9 Hz, 1H), 4,26 (br s, 1H), 3.95 (d, *J* = 9.8 Hz, 1H), 3.15 (*app* s, 2H), 2.10–1.97 (m, 2H), 1.72–1.66 (m, 1H), 1.41–1.34 (m, 1H), 1.28-1.18 (m, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 203.1, 188.3, 151.1, 135.3, 131.8, 129.0, 128.9, 127.4, 127.2, 125.9, 123.0, 119.6, 110.2, 58.6, 56.9, 51.4, 13.8, 12.2, 10.7; **HRMS** (ESI$^+$) calcd for $C_{21}H_{20}NOS$ [MH]$^+$: 334.1260, found: 334.1262 (–0.6 ppm error); **ν_{max}** (thin film)/cm^{-1} 1703, 1604, 1579, 1488, 1237, 740.

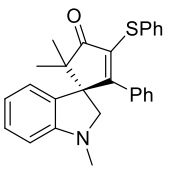
1'-Methyl-2-phenyl-3-(phenylthio)spiro[cyclopentane-1,3'-indolin]-2-en-4-one, 16k



Synthesised using **general procedure D** with thiophenol (32.0 µL, 0.32 mmol), ynone **13k** (54.6 mg, 0.2 mmol) and DCE (2.0 mL). Purification by column chromatography (hexane:EtOAc, 4:1 *v/v*) afforded the *title compound* **16k** (76.0 mg, 99%) as yellow solid, mp 140–142 °C; R_f = 0.44 (hexane:EtOAc, 7:3 *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.18 (m, 8H), 7.08 (d, *J* = 7.5 Hz, 1H), 7.04-7.02 (m, 2H), 6.84 (t, *J* = 7.5 Hz, 1H), 6.55 (d, *J* = 7.9 Hz, 1H), 3.56 (d, *J* = 9.3 Hz, 1H), 3.45 (d, *J* = 9.3 Hz, 1H), 3.05 (d, *J* = 18.2 Hz, 1H), 2.99 (d, *J* = 18.2 Hz, 1H), 2.71 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 203.0, 176.2, 152.5, 135.0, 133.9, 133.5, 132.4, 129.6, 129.3, 129.2, 128.8, 128.4, 127.9, 126.6, 122.3, 118.6, 107.7, 65.6, 55.1, 52.1, 35.4; **HRMS** (ESI$^+$) calcd for $C_{25}H_{21}NNaOS$ [MNa]$^+$: 406.1236, found: 406.1231 (1.2 ppm error); **ν_{max}** (thin film)/cm^{-1}: 1713, 1604, 1490, 740, 697.

1',5,5-Trimethyl-2-phenyl-3-(phenylthio)spiro[cyclopentane-1,3'-indolin]-2-en-4-one, 16l

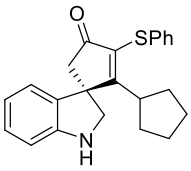


Synthesised using **general procedure D** with thiophenol (23.0 µL, 0.22 mmol), ynone **13l** (42.0 mg, 0.14 mmol) and DCE (2.0 mL). Purification by column chromatography (hexane:EtOAc, 10:1 *v/v*) afforded the *title compound* **16l** (49.0 mg, 85%) as a yellow oil; R_f = 0.59 (hexane:EtOAc, 5:1 *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.15 (m, 9H), 7.03 (s, 1H),6.99 (s, 1H), 6.73–6.68 (m, 2H), 6.51 (d, *J* = 8.0 Hz, 1H), 3.52 (d, *J* = 11.1 Hz, 1H), 3.35 (d, *J* = 11.1 Hz, 1H), 2.07 (s, 3H), 1.33 (s, 3H), 0.91 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 208.6, 174.1, 152.7, 134.2, 133.8, 131.8, 131.0, 129.8, 129.2, 129.1,

128.8, 128.1, 128.0, 126.7, 124.1, 118.1, 107.8, 63.8, 58.6, 53.2, 35.7, 26.9, 19.2; **HRMS** (ESI$^+$) calcd for $C_{27}H_{26}NNaOS$ [MNa]$^+$: 434.1544, found: 434.1549 (1.1 ppm); ν_{max} (thin film)/cm^{-1}: 2970, 1713, 1491, 739, 697.

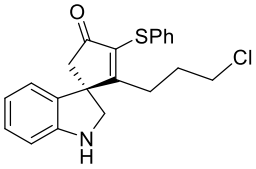
2-cyclopentyl-3-(phenylthio)spiro[cyclopentane-1,3'-indolin]-2-en-4-one, 16m



Synthesised using **general procedure D** with thiophenol (32 µL, 0.32 mmol), ynone **13m** (50.2 mg, 0.2 mmol) and DCE (2 mL). Purification by column chromatography using neutral Fuji Silysia Chromatorex Silica gel (hexane:EtOAc, 10:1→4:1 *v/v*) afforded the *title compound* **16m** (39 mg, 54%) as a pale brown oil. R_f = 0.18 (hexane:EtOAc, 4:1 *v/v*);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.23 (m, 6H), 7.04 (d, J = 7.0 Hz, 1H), 6.91 (td, J = 7.4, 0.9 Hz, 1H), 6.84 (d, J = 7.8 Hz, 1H), 4.03 (d, J = 9.8 Hz, 1H), 3.72 (d, J = 9.8 Hz, 1H), 3.00–2.89 (m, 3H), 2.17–1.90 (m, 5H), 1.73–1.61 (m, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 203.4, 189.9, 151.3, 134.5, 131.7, 131.1, 129.0, 128.9, 127.7, 126.0, 122.8, 119.5, 110.2, 58.0, 56.9, 51.2, 41.0, 33.5, 33.4, 26.9, 26.7; **HRMS** (ESI$^+$) calcd for $C_{23}H_{24}NOS$ [MH]$^+$: 362.1573, found: 362.1581 (-0.8 ppm error); ν_{max} (thin film)/cm^{-1}: 2954, 1705, 1482, 1234, 734.

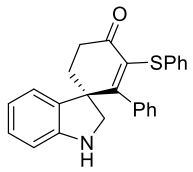
2-(3-chloropropyl)-3-(phenylthio)spiro[cyclopentane-1,3'-indolin]-2-en-4-one, 16n



Synthesised using **general procedure D** with thiophenol (30 µL, 0.29 mmol), ynone **13n** (47 mg, 0.18 mmol) and DCE (1.8 mL). Purification by column chromatography using neutral Fuji Silysia Chromatorex Silica gel (hexane:EtOAc, 10:1→4:1 *v/v*) afforded the *title compound* **16o** (9.9 mg, 15%) as a pale brown oil. R_f = 0.13 (hexane:EtOAc, 4:1 *v/v*);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.12 (m, 6H), 6.88 (d, J = 7.4 Hz, 1H), 6.79–6.73 (m, 2H), 3.92 (br s, 1H), 3.83 (d, J = 9.7 Hz ,1H), 3.71 (d, J = 9.7 Hz, 1H), 3.41–3.33 (m, 2H), 2. 99 (d, J = 19.4 Hz, 1H), 2.75 (d, J = 19.4 Hz, 1H), 2.69–2.61 (m, 2H), 1.87–1.77 (m, 1H), 1.63–1.53 (m, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 203.1, 184.0, 151.2, 133.7, 133.2, 130.6, 129.2, 129.1, 128.8, 126.6, 122.8, 119.6, 110.4, 57.8, 55.5, 50.0, 44.7, 31.4, 27.1; **HRMS** (ESI$^+$) calcd for $C_{21}H_{21}ClNOS$ [MH]$^+$: 370.1023, found: 370.1027 (1.8 ppm error); ν_{max} (thin film)/cm^{-1}: 2924, 2855, 1712, 1483, 743.

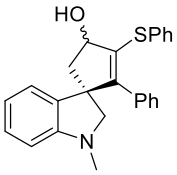
2-Phenyl-3-(phenylthio)spiro[cyclohesane-1,3'-indolin]-2-en-4-one, 16p



Synthesised using **general procedure D** with thiophenol (32.0 µL, 0.49 mmol), ynone **13p** (82.0 mg, 0.3 mmol) and DCE (3.0 mL). Purification by column chromatography (hexane:EtOAc, *7*:3 *v/v*) afforded the *title compound* **16p** (34.5 mg, 30%) as a yellow oil; R_f = 0.23 (hexane:EtOAc, 7:3 *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.10 (m, 11H), 6.82 (t, *J* = 7.1 Hz, 2H), 6.63 (d, *J* = 7.8 Hz, 2H), 3.61 (d, *J* = 9.3 Hz, 1H), 3.35 (d, *J* = 9.3 Hz, 1H), 2.88 (ddd, *J* = 17.5, 12.5, 4.8 Hz, 1H), 2.65 (dt, *J* = 17.5, 4.8 Hz, 1H), 2.50 (dt, *J* = 12.5, 4.8 Hz, 1H), 2.39 (td, *J* = 12.5, 4.8 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 194.3, 168.1, 150.9, 138.7, 136.5, 134.1, 129.8, 129.1, 128.7, 128.7, 127.9, 127.8, 127.0, 125.9, 124.4, 118.8, 110.7, 58.9, 53.4, 34.84, 34.80; **HRMS** (ESI$^+$) calcd for $C_{25}H_{21}NNaOS$ [MNa]$^+$: 406.1236, found: 406.1236 (0.1 ppm error); ν_{max} (thin film)/cm^{-1}: 1682, 1485, 740, 698.

1'-Methyl-2-phenyl-3-(propylthio)spiro[cyclopentane-1,3'-indolin]-2-en-4-ol, 16q



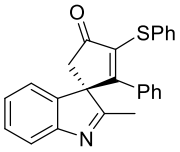
Synthesised using **general procedure D** with thiophenol (68.6 µL, 0.672 mmol), ynone **13q** (115.6 mg, 0.42 mmol), and DCE (4.2 mL). Purification by column chromatography (hexane:EtOAc, 10:1 → 5:1 *v/v*) afforded the *title compound* **16q** as a mixture of diastereoisomers (45.3 mg, 28%), as yellow oil; R_f = 0.40 (*diastereoisomer I*) and R_f = 0.21 (*diastereoisomer II*) (hexane:EtOAc, 4:1, *v/v*);

^{1}H NMR for diastereoisomer I (400 MHz, $CDCl_3$) δ 7.40–7.11 (m, 10H), 6.97 (d, *J* = 7.5Hz, 2H), 6.76 (td, *J* = 7.5, 2.0 Hz, 1H), 6.42 (d, *J* = 7.8 Hz, 1H), 4.80 (d, *J* = 7.0 Hz, 1H), 3.40 (d, *J* = 9.0 Hz, 1H), 3.25 (d, *J* = 9.0 Hz, 1H), 2.62 (s, 3H), 2.52 (dd, *J* = 14.2, 7.0 Hz, 1H), 2.38 (dd, *J* = 14.2, 2.8 Hz, 1H), 2.17 (d, *J* = 2.8 Hz, 1H); **^{13}C{^{1}H} NMR** for diasteroisomer I (100 MHz, $CDCl_3$) 152.3, 152.0, 135.0, 134.6, 133.6, 130.4, 129.1, 128.6, 128.3, 127.8, 127.7, 127.0, 124.3, 118.3, 107.3, 99.9, 74.8, 66.3, 59.9, 48.1, 35.7; **HRMS** (ESI) calcd for $C_{25}H_{24}NOS$ $[MH]^+$: 386.1574, found: 386.1573 (0.2 ppm); ν_{max} (thin film)/cm^{-1}: 2925, 1603, 1490, 741, 697.

^{1}H NMR for distereoisomer II (400 MHz, $CDCl_3$) δ 7.43-7.40 (m, 2H), 7.33–7.13 (m, 7H), 7.08 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.01-6.97 (m, 2H), 6.74 (td, *J* = 7.3, 1.1 Hz, 1H), 6.46 (d, *J* = 8.0 Hz, 1H), 4.93 (app t, *J* = 5.6 Hz, 1H), 3.43 (d, *J* = 9.4 Hz, 1H), 3.31 (d, *J* = 9.4 Hz, 1H), 2.80 (dd, *J* = 13.5, 7.0 Hz, 1H), 2.64 (s, 3H), 2.22 (dd, *J* = 13.5, 5.8 Hz, 1H), 2.14 (s broad, 1H); **^{13}C{^{1}H} NMR** for diastereoisomer II (100 MHz, $CDCl_3$) δ 152.5, 150.6, 135.9, 134.84, 134.79, 133.0, 131.1, 129.2, 129.0, 128.5, 127.8, 127.7, 127.3, 122.5, 117.9, 107.5, 74.6, 66.8, 59.2, 49.3, 35.5; **HRMS** (APCI) calcd for $C_{25}H_{24}NOS$ $[MH]^+$: 386.1572, found: 386.1573 (0.4 ppm); ν_{max} (thin film)/cm^{-1}: 2855, 1604, 1491, 742, 696.

*Note: the yield of **16q** can be improved to 64% with the addition of* **13k** *(20 mol%) into the reaction as a radical initiator.*

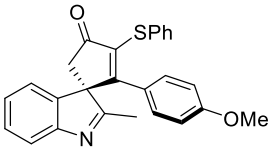
2'-Methyl-2-phenyl-3-(phenylthio)spiro[cyclopentane-1,3'-indol]-2-en-4-one, 18a



Synthesised using **general procedure E** with thiophenol (16.0 µL, 0.16 mmol), $Ru(bpy)_3(PF)_2$ (1.0 mg, 1 mol%), ynone **13a** (27.3 mg, 0.1 mmol) and MeCN (1.0 mL). Purification by column chromatography (hexane:EtOAc, 3:2 *v/v*) afforded the *title compound* **18a** (29.0 mg, 68%) as a yellow solid. Mp: 59–60 °C; R_f = 0.29 (hexane:EtOAc, 3:2 *v/v*).

H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 7.7 Hz, 1H), 7.33–7.27 (m, 1H), 7.21–7.07 (m, 7H), 7.01 (*app* t, J = 7.7 Hz, 2H), 6.74 (d, J = 7.8 Hz, 2H), 2.85 (d, *J* = 19.2 Hz, 1H), 2.77 (d, J = 19.2 Hz, 1H), 2.13 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) 201.2, 181.4, 171.5, 155.1, 140.7, 137.2, 132.6, 132.4, 130.3, 130.1 129.2, 129.0, 128.3, 127.1, 127.0, 126.5, 121.7, 120.7, 67.1, 43.3, 16.0; **HRMS** (ESI^+) calcd for $C_{25}H_{19}NNaOS$ $[MNa]^+$: 404.1080, found: 404.1079 (0.1 ppm error); ν_{max} (thin film)/cm^{-1}: 1716, 1580, 1461, 1441, 740, 697.

2-(4-Methoxyphenyl)-2'-methyl-3-(phenylthio)spiro[cyclopentane-1,3'-indol]-2-en-4-one, 18b

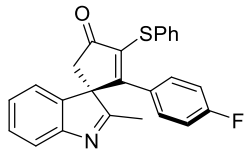


Synthesised using general **procedure D** with thiophenol (32.0 µL, 0.32 mmol), $Ru(bpy)_3(PF)_2$ (1.7 mg, 0,002 mmol), ynone **13b** (60.6 mg, 0.2 mmol) and MeCN (2 mL). Purification by column chromatography (hexane:EtOAc, 3:2 *v/v*) afforded the *title compound* **18b** (55.0 mg, 67%) as a yellow solid. Mp 64–65 °C; R_f = 0.26 (hexane:EtOAc, 3:*2 v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.7 Hz, 1H), 7.31 (td, *J* = 6.8, 2.2 Hz, 1H), 7.22–7.07(m, 7H), 6.80 (*app* d, *J* = 8.9 Hz, 2H), 6.54 (*app* d, *J* = 8.9 Hz, 2H), 3.61 (s, 3H), 2.81 (d, *J* = 18.5 Hz, 1H), 2.72 (d, *J*

= 18.5 Hz, 1H), 2.10 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 201.1, 182.2, 171.3, 161.3, 155.0, 141.4, 134.9, 133.1, 129.5, 129.2, 129.1, 129.0, 126.9, 126.6, 124.8, 121.7, 120.8, 113.8, 67.0, 55.2, 43.6, 15.9; **HRMS** (ESI$^+$) calcd for $C_{26}H_{21}NNaO_2S$ [MNa]$^+$: 434.1185, found: 434.1180 (1.2 ppm error); $\mathbf{\nu_{max}}$ (thin film)/cm^{-1} : 1711, 1603, 1578, 1505, 1253, 1178, 1025, 907, 726, 688.

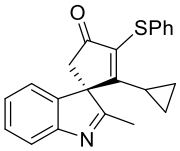
2-(4-Fluorophenyl)-2'-methyl-3-(phenylthio)spiro[cyclopentane-1,3'-indol]-2-en-4-one, 18c



Synthesised using **general procedure E** with thiophenol (32.0 µL, 0.32 mmol), $Ru(bpy)_3(PF)_2$ (1.7 mg, 1 mol%), ynone **13c** (58.2 mg, 0.2 mmol) and MeCN (2 mL). Purification by column chromatography (hexane:EtOAc, 3:2 *v/v*) afforded the *title compound* **18c** (49 mg, 61%) as a yellow solid. Mp: 54–56 °C; R_f = 0.26 (hexane:EtOAc, 3:2 *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.6 Hz, 1H), 7.26 (dt, *J* = 6.6, 2.2 Hz, 1H), 7.15–7.03 (m, 7H), 6.71–6.63 (m, 4H), 2.80 (d, *J* = 18.5 Hz, 1H), 2.72 (d, *J* = 18.5 Hz, 1H), 2.08 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 201.0, 181.3, 169.7, 163.5 (d, J^1 = 252.4 Hz), 155.0, 140.6, 137.3, 132.2, 130.2, 129.3, 129.3, 129.2 (d, J^3 = 9.0 Hz), 128.4 (d, J^4 = 3.5 Hz), 127.3, 126.6, 121.7, 120.8, 115.5 (d, J^2 = 22.0 Hz, 1H), 67.1, 43.2, 15.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (-108.63)–(-108.70) (m, 1F); **HRMS** (ESI$^+$) calcd for $C_{25}H_{19}FNOS$ [MH]$^+$: 400.1166, found: 400.1168 (-0.5 ppm error); $\mathbf{\nu_{max}}$ (thin film)/cm^{-1}: 1716, 1602, 1580, 1503, 1236, 1161, 757, 739.

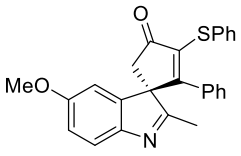
2-Cyclopropyl-2'-methyl-3-(phenylthio)spiro[cyclopentane-1,3'-indol]-2-en-4-one, 18d



Synthesised using **general procedure E** with thiophenol (32.0 µL, 0.32 mmol), $Ru(bpy)_3(PF)_2$ (1.7 mg, 1 mol%), ynone **13d** (47.4 mg, 0.2 mmol) and MeCN (2.0 mL). Purification by column chromatography (hexane:EtOAc, 3:2 *v/v*) afforded the *title compound* **18d** (26.0 mg, 38%) as a yellow solid. Mp: 60–62°C; R_f = 0.25 (hexane:EtOAc, 3:2 *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.9 Hz, 1H), 7.38 (dt, *J* = 7.4, 1.5, 1H), 7.27–7.16 (m, 7H), 2.74 (d, *J* = 19.0 Hz, 1H), 2.69 (d, *J* = 19.0 Hz, 1H), 2.25 (s, 3H), 1.26–1.16 (m, 2H), 0.93–0.73 (m, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 201.1, 182.9, 182.0, 155.2, 140.6, 134.3, 132.2, 129.2, 129.2, 128.3, 126.6, 126.5, 121.9, 120.7, 67.3, 42.4, 15.9, 14.0, 11.5, 10.0; **HRMS** (ESI$^+$) calcd for $C_{22}H_{20}NOS$ [MH]$^+$: 346.1260, found: 346.1261 (–0.2 ppm error); $\mathbf{\nu_{max}}$ (thin film)/cm^{-1} 1713, 1579, 741.

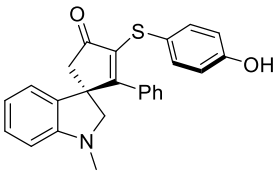
5'-Methoxy-2'-methyl-2-phenyl-3-(phenylthio)spiro[cyclopentane-1,3'-indol]-2-en-4-one, 18e



Synthesised using **general procedure E** with thiophenol (32.0 µL, 0.32 mmol), $Ru(bpy)_3(PF)_2$ (1.7 mg, 1 mol%), ynone **13e** (60.6 mg, 0.2 mmol) and MeCN (2.0 mL). Purification by column chromatography (hexane:EtOAc, 3:2 *v/v*) afforded the *title compound* **18e** (43.0 mg, 53%) as a yellow solid. Mp: 59–61 °C; R_f = 0.25 (hexane:EtOAc, 3:2 *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.5 Hz, 1H), 7.18–7.01 (m, 7H), 6.78–6.74 (m, 3H), 6.66 (d, *J* = 2.4 Hz, 1H), 3.67 (s, 3H), 2.81 (d, *J* = 19.1 Hz, 1H), 2.70 (d, *J* = 19.1 Hz, 1H), 2.06 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 201.2, 179.0, 171.6, 158.8, 148.7, 142.4, 137.0, 132.6, 132.4, 130.4, 130.1, 129.0, 128.3, 127.1, 127.1, 121.1, 113.8, 108.1, 67.2, 55.7, 43.6, 15.8; **HRMS** (ESI$^+$) calcd for $C_{26}H_{21}NO_2S$ [MH]$^+$: 412.1366, found: 412.1368 (-0.6 ppm error); $\mathbf{\nu_{max}}$ (thin film)/cm^{-1} 1716, 1581, 1473, 1440, 1284, 739, 690.

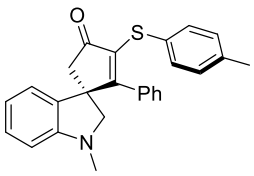
3-((4-Hydroxyphenyl)thio)-1'-methyl-2-phenylspiro[cyclopentane-1,3'-indolin]-2-en-4-one, 19a



Synthesised using **general procedure D** with 4-mercaptophenol (40.0 mg, 0.32 mmol), ynone **13k** (54.6 mg, 0.2 mmol) and DCE (2.0 mL). Purification by column chromatography (hexane:EtOAc, 7:3 *v/v*) afforded the *title compound* **19a** (68.0 mg, 85%) as a yellow solid. Mp: 168–170 °C; R_f = 0.26 (hexane:EtOAc, 7:3 *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.16 (m, 7H), 6.96-6.93 (m, 3H), 6.75 (t, *J* = 7.1 Hz, 1H), 6.63 (d, *J* = 8.7 Hz, 2H), 6.47 (d, *J* = 7.1 Hz, 1H), 5.16 (s, 1H), 3.46 (d, *J* = 9.6 Hz, 1H), 3.36 (d, *J* = 9.6 Hz, 1H), 2.94 (d, *J* = 18.8 Hz, 1H), 2.89 (d, *J* = 18.8 Hz, 1H), 2.64 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 203.7, 174.6, 173.3, 155.3, 152.4, 136.4, 134.0, 133.4, 132.5, 129.2, 128.4, 127.9, 123.3, 122.2, 118.5, 116.0, 107.7, 65.5, 54.9, 52.2, 35.4; **HRMS** (ESI$^+$) calcd for $C_{25}H_{22}NO_2S$ [MH]$^+$: 400.1366, found: 400.1365 (0.3 ppm error); ν_{max} (thin film)/cm^{-1} 3372, 1697, 1602, 1582, 1493, 1268, 1218, 830, 743, 697.

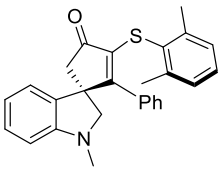
1'-Methyl-2-phenyl-3-(p-tolylthio)spiro[cyclopentane-1,3'-indolin]-2-en-4-one, 19b



Synthesised using **general procedure D** with 4-methylbenzenethiol (27.3 mg, 0.22 mmol), ynone **13k** (54.6 mg, 0.2 mmol) and DCE (2 mL). Purification by column chromatography (hexane:EtOAc, 4:1 *v/v*) afforded the *title compound* **19b** (72.0 mg, 91%) as a yellow solid. Mp: 125–127 °C; R_f = 0.34 (hexane:EtOAc, 4:1 *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) 7.24-7.10 (m, 6H), 6.97-6.91 (m, 5H), 6.72 (td, *J* = 7.6, 2.4 Hz, 1H), 6.57 (d, *J* = 7.9 Hz, 1H), 3.43 (d, *J* = 9.4 Hz, 1H), 3.33 (d, *J* = 9.4 Hz, 1H), 2.91 (d, *J* = 18.9 Hz, 1H), 2.84 (d, *J* = 18.9 Hz, 1H), 2.59 (s, 3H), 2.22 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) 203.1, 175.3, 152.4, 136.8, 135.5, 133.9, 132.5, 130.2, 129.8, 129.6, 129.2, 129.1, 128.4, 127.9, 122.2, 118.5, 107.6, 65.6, 54.9, 52.2, 35.4, 21.0; **HRMS** (ESI$^+$) calcd for $C_{26}H_{23}NNaOS$ [MNa]$^+$: 420.1393, found: 420.1389 (0.9 ppm error); ν_{max} (thin film)/cm^{-1}: 1712, 1603, 1489, 804, 741, 697, 493.

3-((2,6-Dimethylphenyl)thio)-1'-methyl-2-phenylspiro[cyclopentane-1,3'-indolin]-2-en-4-one, 19c

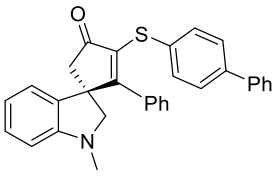


Synthesised using **general procedure D** with 2,6-dimethylthiophenol (46.6 mg, 0.32 mmol), ynone **13k** (54.6 mg, 0.2 mmol) and DCE (2.0 mL). Purification by column chromatography using hexane:EtOAc (5:1 → 4:1, *v/v*) afforded the *title compound* **19c** (74.0 mg, 90%) as a yellow solid. Mp: 125–127 °C; R_f = 0.35 (hexane:EtOAc, 4:1 *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18–7.15 (m ,2H), 7.12–7.08 (m, 2H), 7.05 (d, *J* = 7.7 Hz, 1H), 6.81 (d, *J* = 7.3 Hz, 2H), 6.77 (t, *J* = 7.2 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 2H), 6.83–6.75 (m, 3H), 6.43 (d, *J* = 8.0 Hz, 1H), 3.42 (d, *J* = 8.9 Hz, 1H), 3.31 (d, *J* = 8.9 Hz, 1H), 2.92 (d, *J* = 19.1 Hz, 1H), 2.86 (d, *J* = 19.1 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 202.9, 169.7, 152.6, 142.3, 135.8, 133.7, 132.4, 129.0, 128.9, 128.5, 128.4, 127.8, 127.6, 127.5, 122.4, 118.3, 107.6, 65.7, 54.8, 51.4, 35.3, 22.1; **HRMS** (ESI$^+$) calcd for $C_{27}H_{26}NOS$ [MH]$^+$: 412.1729, found: 412.1729 (0.2 ppm); ν_{max} (thin film)/cm^{-1}: 1708, 1490, 1460, 773, 742, 699.

3-([1,1'-Biphenyl]-4-ylthio)-1'-methyl-2-phenylspiro[cyclopentane-1,3'-indolin]-2-en-4-one, 19d

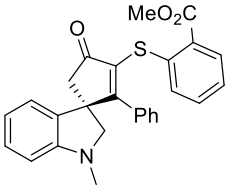
Synthesised using **general procedure D** with [1,1'-biphenyl]-4-thiol (48.0 mg, 0.26 mmol), ynone **13k** (54.6 mg, 0.20 mmol) and DCE (2.0 mL). Purification by column chromatography (hexane:Et_2O, 7:3 *v/v*)



afforded the *title compound* **19d** (91.9 mg, 99%) as a yellow solid, mp: 141–143 °C; R_f = 0.22 (hexane:Et_2O, 7:3 *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.50 (m, 2H), 7.46–7.39 (m, 4H), 7.37–7.24 (m, 4H), 7.24–7.16 (m, 3H), 7.04 (dd, *J* = 7.4, 1.0 Hz, 1H), 7.01–6.96 (m, 2H), 6.78 (td, *J* = 7.4, 0.8 Hz, 1H), 6.49 (d, *J* = 7.9 Hz, 1H), 3.51 (d, *J* = 9.5 Hz, 1H), 3.40 (d, *J* = 9.5 Hz, 1H), 3.03(d, *J* = 18.7 Hz, 1H), 2.97 (d, *J* = 18.7 Hz, 1H), 2.65 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 203.2, 176.2, 152.6, 140.4, 139.7, 135.0, 133.9, 132.5, 132.4, 130.1, 129.4, 129.3, 128.8, 128.5, 128.0, 127.6, 127.4, 127.0, 122.3, 118.6, 107.8, 65.7, 55.2, 52.2, 35.4; **HRMS** (ESI$^+$) calcd for $C_{31}H_{25}NNaOS^+$ [MNa]$^+$: 482.1549, found: 482.1556 (-0.3 ppm error); ν_{max} (thin film)/cm^{-1}: 1714, 1603, 1490, 1479, 760, 743, 697.

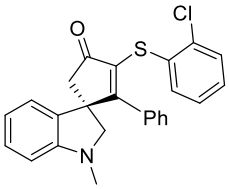
Methyl 2-((1'-methyl-4-oxo-2-phenylspiro[cyclopentane-1,3'-indolin]-2-en-3-yl)thio)benzoate, 19e



Synthesised using **general procedure D** with methyl thiosalicylate (53.8 mg, 0.32 mmol), ynone **13k** (54.6 mg, 0.2 mmol) and 1,2-dichloroethane (2.0 mL). Purification by column chromatography (hexane:EtOAc, 5:1→3:1 *v/v*) afforded the *title compound* **19e** (48.0 mg, 54%) as a yellow solid. Mp: 149–151 °C; R_f = 0.14 (hexane:EtOAc, 3:1 *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.37 (td, *J* = 7.6, 1.6 Hz, 1H), 7.30–7.26 (m, 1H), 7.23–7.18 (m, 4H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.7 Hz, 1H), 7.04–7.02 (m, 2H), 6.79 (*app* t, *J* = 7.4 Hz, 1H), 6.51 (t, *J* = 7.7 Hz, 1H), 3.89 (s, 3H), 3.55 (d, *J* = 9.1 Hz, 1H), 3.44 (d, *J* = 9.1 Hz, 1H), 3.05 (d, *J* = 18.7 Hz, 1H), 2.98 (d, *J* = 18.7 Hz, 1H), 2.67 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 202.9, 179.2, 166.6, 152.5, 138.6, 134.3, 133.7, 132.3, 132.2, 131.5, 129.6, 129.3, 128.3, 128.0, 127.8, 127.4, 125.0, 122.3, 118.6, 107.8, 65.7, 55.4, 52.2, 52.2, 35.4; **HRMS** (ESI$^+$) calcd for $C_{27}H_{24}NO_3S$ [MH]$^+$: 442.1472, found: 442.1471 (0.2 ppm); **ν_{max}** (thin film)/cm^{-1}: 1713, 1270, 1254, 741.

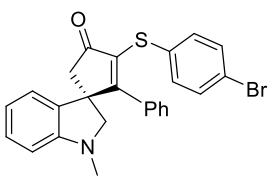
3-((2-Chlorophenyl)thio)-1'-methyl-2-phenylspiro[cyclopentane-1,3'-indolin]-2-en-4-one, 19f



Synthesised using **general procedure D** with 2-chlorobenzenethiol (49.0 mg, 0.26 mmol), ynone **13k** (37.6 mg, 0.20 mmol) and DCE (2.0 mL). Purification by column chromatography (hexane:Et_2O, 3:2 *v/v*) afforded the *title compound* **19f** (72.0 mg, 86%) as a yellow solid. Mp: 149–151 °C; R_f = 0.18 (hexane:Et_2O, 3:2 *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.22 (m, 2H), 7.21–7.15 (m, 4H), 7.11–7.05 (m, 3H), 6.98–6.93 (m, 2H), 6.77 (td, *J* = 7.4, 1.0 Hz, 1H), 6.47 (d, *J* = 7.9 Hz, 1H), 3.49 (d, *J* = 9.4 Hz, 1H), 3.38 (d, J = 9.4 Hz, 1H), 3.00 (d, *J* = 18.7 Hz, 1H), 2.94 (d, *J* = 18.7 Hz, 1H), 2.63 (s, 3H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 202.6, 175.9, 152.6, 134.5, 134.0, 133.8, 132.3, 132.1, 131.3, 129.9, 129.4, 129.3, 128.2, 128.0, 128.0, 126.9, 122.6, 118.7, 107.9, 65.8, 55.3, 52.1, 35.5; HRMS (ESI$^+$) calcd for $C_{25}H_{20}ClNNaOS$ [MNa]$^+$: 440.0846, found: 440.0833 (2.8 ppm error); **ν_{max}** (thin film)/cm^{-1}: 1714, 1604, 1490, 1451, 743, 698.

3-((4-Bromophenyl)thio)-1'-methyl-2-phenylspiro[cyclopentane-1,3'-indolin]-2-en-4-one, 19g

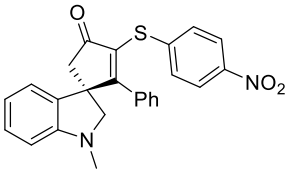


Synthesised using **general procedure D** with 4-bromobenzenethiol (49.0 mg, 0.26 mmol), ynone **13k** (54.6 mg, 0.20 mmol) and DCE (2.0 mL). Purification by column chromatography (hexane:Et_2O, 3:2 *v/v*) afforded the *title compound* **19g** (90.0 mg, 97%) as a yellow solid. Mp: 120–122 °C; R_f = 0.23 (hexane:Et_2O, 3:2 *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.25 (m, 3H), 7.23–7.16 (m, 3H), 7.12–7.07 (m, 2H), 6.98 (dd, *J* = 7.4, 1.0 Hz, 1H), 6.95–6.91 (m, 2H), 6.77 (td, *J* = 7.4, 0.9 Hz, 1H), 6.48 (d, *J* = 7.9 Hz, 1H), 3.49 (d, *J* = 9.5 Hz,

1H), 3.38 (d, *J* = 9.5 Hz, 1H), 2.98 (d, *J* = 18.7 Hz, 1H), 2.91 (d, *J* = 18.7 Hz, 1H), 2.64 (s, 3H); **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 202.9, 176.6, 152.6, 134.6, 133.8, 132.7, 132.2, 132.0, 131.5, 129.6, 129.4, 128.4, 128.1, 122.3, 120.8, 118.7, 107.8, 65.6, 55.2, 52.1, 35.4; **HRMS** (ESI^+) calcd for $C_{25}H_{20}BrNNaOS$ $[MNa]^+$: 484.0341, found: 484.0343 (-0.7 ppm error); ν_{max} (thin film)/cm^{-1}: 1715, 1604, 1490, 1472, 743, 697.

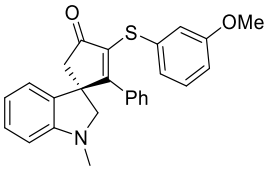
1'-Methyl-3-((4-nitrophenyl)thio)-2-phenylspiro[cyclopentane-1,3'-indolin]-2-en-4-one, 19h



Synthesised using **general procedure D** with 4-nitrothiophenol (49.8 mg, 0.32 mmol), ynone **13k** (54.6 mg, 0.2 mmol) and DCE (2 mL). Purification by column chromatography (hexane:EtOAc, 5:1 *v/v*) to afford the *title compound* **19h** (36.0 mg, 42%) as a yellow oil; R_f = 0.16 (hexane:EtOAc, 5:1 *v/v*).

^1H NMR (400 MHz, $CDCl_3$) δ 8.05–8.02 (m, 2H), 7.30–7.17 (m, 6H), 7.00 (*app* t, *J* = 7.5 Hz, 1H), 6.94–6.91 (m, 2H), 6.78 (dt, *J* = 7.4, 1.0 Hz, 1H), 3.51 (d, *J* = 9.6 Hz, 1H), 3.41 (d, *J* = 9.6 Hz, 1H), 3.04 (d, *J* = 18.6 Hz, 1H), 2.95 (d, *J* = 18.6 Hz, 1H), 2.63 (s, 3H); **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 202.2, 179.5, 152.5, 145.8, 143.7, 133.3, 132.1, 131.6, 130.0, 129.6, 128.2, 128.1, 127.8, 124.0, 122.1, 118.7, 107.9, 65.5, 55.5, 51.9, 35.3; **HRMS** (ESI^+) calcd for $C_{25}H_{21}N_2O_3S$ $[MH]^+$: 429.1267, found: 429.1266 (0.4 ppm error); ν_{max} (thin film)/cm^{-1}: 1714, 1513, 1490, 852, 740, 697.

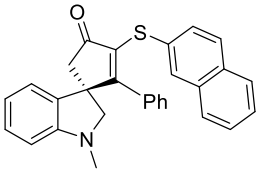
3-((3-Methoxyphenyl)thio)-1'-methyl-2-phenylspiro[cyclopentane-1,3'-indolin]-2-en-4-one, 19i



Synthesised using **general procedure D** with 3-methoxythiophenol (44.9 mg, 0.32 mmol), ynone **13k** (54.6 mg, 0.2 mmol) and DCE (2.0 mL). Purification by column chromatography (hexane:EtOAc, 3:1 *v/v*) to afford the *title compound* **19i** (74.5 mg, 90%) as a yellow oil; R_f = 0.37 (hexane:EtOAc, 3:1 *v/v*).

^1H NMR (400 MHz, $CDCl_3$) δ 7.51–7.47 (m, 3H), 7.4 (*app* t, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.32 (app d, *J* = 7.8 Hz, 1H), 7.12-7.04 (m, 3H), 6.97 (dd, *J* = 8.4. 2.0 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 4.02 (s, 3H), 3.80 (d, *J* = 9.3 Hz, 1H), 3.69 (d, *J* = 9.3 Hz, 1H), 3.29 (d, *J* = 18.9 Hz, 1H), 3.23 (d, *J* = 18.9 Hz, 1H), 2.94 (s, 3H); **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 203.0, 176.5, 159.6, 152.4, 134.7, 133.8, 132.3, 129.6, 129.3, 129.2, 128.3, 127.9, 122.2, 121.7, 118.5, 114.8, 112.5, 107.7, 35.3; **HRMS** (ESI^+) calcd for $C_{26}H_{23}NNaO_2S$ $[MNa]^+$: 436.1341, found: 436.1342 (0.3 ppm); ν_{max} (thin film)/cm^{-1}: 1712, 1589, 1477, 1245, 1229, 728, 696.

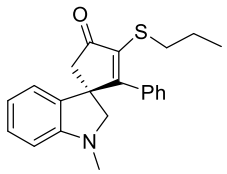
1'-Methyl-3-(naphthalen-2-ylthio)-2-phenylspiro[cyclopentane-1,3'-indolin]-2-en-4-one, 19j



Synthesised using **general procedure D** with 2-napthylthiol (42 mg, 0.26 mmol), ynone **13k** (54.6 mg, 0.20 mmol) and DCE (2.0 mL). Purification by column chromatography (hexane:Et_2O, 7:3 *v/v*) afforded the *title compound* **19j** (86.7 mg, 99%) as a yellow solid, mp: 129–133 °C; Rf = 0.22 (hexane:Et_2O, 7:3 *v/v*).

^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.5 Hz, 1H), 7.71–7.64 (m, 3H), 7.49–7.37 (m, 3H), 7.31 (dd, *J* = 8.7, 1.2 Hz, 1H), 7.26–7.12 (m, 4H), 7.07 (d, *J* = 7.3 Hz, 1H), 7.03– 6.94 (m, 2H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.49 (d, *J* = 7.9 Hz, 1H), 3.52 (d, *J* = 9.3 Hz, 1H), 3.41 (d, *J* = 9.3 Hz, 1H), 3.02 (d, *J* = 18.7 Hz, 1H), 2.95 (d, *J* = 18.7 Hz, 1H), 2.65 (s, 3H); **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 203.2, 176.6, 152.6, 135.0, 133.9, 133.6, 132.5, 132.1, 130.8, 129.4, 129.3, 128.6, 128.6, 128.4, 128.0, 127.7, 127.5, 127.3, 126.5, 126.0, 122.4, 118.6, 107.8, 65.6, 55.2, 52.2, 35.4; **HRMS (ESI+)** calcd for $C_{29}H_{23}NNaOS^+$ $[MNa]^+$: 456.1393, found: 456.1395 (–1.0 ppm error); ν_{max} (thin film)/cm^{-1}: 1714, 1604, 1490, 742, 698.

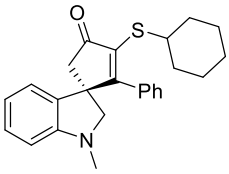
5'-Methoxy-2'-methyl-2-phenyl-3-(phenylthio)spiro[cyclopentane-1,3'-indol]-2-en-4-one, 19k



Synthesised using **general procedure D** with 1-propanethiol (30.0 µL, 0.32 mmol), ynone **13k** (54.6 mg, 0.2 mmol) and DCE (2.0 mL). Purification by column chromatography (hexane:EtOAc, 4:1 *v/v*) afforded the *title compound* **19k** (63.0 mg, 90%) as a yellow solid. Mp: 85–86 °C; R_f = 0.40 (hexane:EtOAc, 4:1 *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.21 (m, 3H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 2H), 6.94 (d, J = 7.5 Hz, 1H), 6.71(t, J = 7.3 Hz, 1H), 6.43 (d, *J* = 7.9 Hz, 1H), 3.39 (d, *J* = 9.6 Hz, 1H), 3.30 (d, *J* = 9.6 Hz, 1H), 2.89-2.82 (m, 3H), 2.75-2.70 (m, 1H), 2.60 (s, 3H), 1.53-1.42 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) 204.4, 172.2, 152.4, 135.8, 134.4, 132.8, 129.1, 129.0, 128.4, 127.9, 122.2, 118.5, 107.6, 65.6, 54.7, 52.3, 35.4, 33.0, 23.3, 13.1; **HRMS** (ESI$^+$) calcd for $C_{22}H_{24}NOS$ [MH]$^+$: 350.1573, found: 350.1577 (-1.1 ppm error); $\mathbf{\nu_{max}}$ (thin film)/cm^{-1}:1707, 1604, 1490, 743, 698.

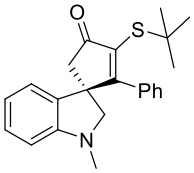
3-(Cyclohexylthio)-1'-methyl-2-phenylspiro[cyclopentane-1,3'-indolin]-2-en-4-one, 19l



Synthesised using **general procedure D** with cyclohexanethiol (39.0 µL, 0.32 mmol), ynone **13k** (54.6 mg, 0.2 mmol) and DCE (2.0 mL). Purification by column chromatography (hexane:EtOAc, 4:1 *v/v*) afforded the *title compound* **19l** (57.7 mg, 74%) as a yellow oil; R_f = 0.31 (hexane:EtOAc, 4:1 *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.24 (m, 3H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.00–6.97 (m, 3H), 6.75 (t, *J* = 7.4 Hz, 1H), 6.47 (d, *J* = 7.9 Hz, 1H), 3.57–3.50 (m, 1H), 3.43 (d, *J* = 9.4 Hz, 1H), 3.34 (d, *J* = 9.4 Hz, 1H), 2.92 (*app* s, 2H), 2.64 (s, 3H), 1.89–1.81 (m, 2H), 1.69-1.55 (m, 3H), 1.26–1.13 (m, 5H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) 204.6, 173.1, 152.4, 135.4, 134.5, 132.8, 129.0, 128.4, 127.9, 122.2, 118.5, 107.6, 65.6, 54.8, 52.2, 42.4, 35.4, 33.5, 33.3, 25.8, 25.6; **HRMS** (ESI$^+$) calcd for $C_{25}H_{27}NNaOS$ [MNa]$^+$: 412.1706, found: 412.1703 (0.6 ppm error); $\mathbf{\nu_{max}}$ (thin film)/cm^{-1}: 1704, 1603, 1489, 730, 696.

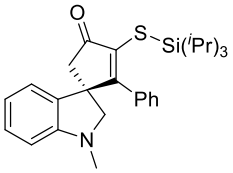
3-(*tert*-Butylthio)-1'-methyl-2-phenylspiro[cyclopentane-1,3'-indolin]-2-en-4-one, 19m



Synthesised using **general procedure D** with *tert*-butylthiol (28.8 mg, 0.32 mmol), ynone **13k** (54.6 mg, 0.2 mmol) and DCE (2.0 mL). Purification by column chromatography (hexane:EtOAc:CH_2Cl_2, 7:2:1 *v/v/v*) afforded the *title compound* **19m** (27.0 mg, 37%) as orange oil; R_f = 0.45 (hexane:EtOAc:CH_2Cl_2, 7:2:1 *v/v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.20 (m, 4H), 7.05–6.99 (m, 3H), 6.80 (t, *J* = 7.8 Hz, 1H), 6.50 (d, *J* = 7.9 Hz, 1H), 3.47 (d, *J* = 9.2 Hz, 1H), 3.38 (d, *J* = 9.2 Hz, 1H), 3.03 (d, *J* = 19.0 Hz, 1H), 2.93 (d, *J* = 19.0 Hz, 1H), 2.65 (s, 3H), 1.22 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 205.8, 182.5, 152.6, 134.8, 134.6, 132.5, 129.2, 129.1, 129.0, 127.6, 122.2, 118.4, 107.7, 65.6, 55.2, 51.6, 48.8, 35.3, 31.5; **HRMS** (ESI$^+$) calcd for $C_{23}H_{26}NOS$ [MH]$^+$: 364.1730, found: 364.1730 (-0.2 ppm error); $\mathbf{\nu_{max}}$ (thin film)/cm^{-1}:1713, 1604, 1490, 742, 698.

1'-Methyl-2-phenyl-3-((triisopropylsilyl)thio)spiro[cyclopentane-1,3'-indolin]-2-en-4-one, 19n

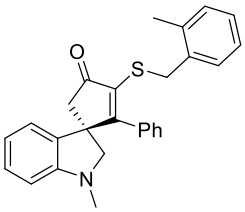


Synthesised using **general procedure D** with triisopropylsilanethiol (68.0 µL, 0.32 mmol), ynone **13k** (54.6 mg, 0.2 mmol) and DCE (2.0 mL). Purification by column chromatography (hexane:EtOAc, 10:1 → 5:1 *v/v*) afforded the *title compound* **19n** (33.4 mg, 36%) as a yellow oil; R_f = 0.21 (hexane:EtOAc, 10:1 *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.22 (m, 5H), 7.17 (td, *J* = 7.4, 1.1 Hz, 1H), 7.10–7.08 (m, 2H), 6.98 (dd, *J* = 7.4, 1.0 Hz, 1H), 6.73 (*app* t, *J* = 7.4 Hz, 1H), 6.45 (d, *J* = 7.8 Hz, 1H), 3.41 (d, *J* = 7.8 Hz, 1H), 3.30

(d, *J* = 9.4 Hz, 1H), 2.93 (d, *J* = 18.3 Hz, 1H), 2.88 (d, *J* = 18.3 Hz, 1H), 2.61 (s, 3H), 1.29-1.20 (m, 3H), 1.06 (d, *J* = 7.4 Hz, 9H), 1.01 (d, *J* = 7.4 Hz, 9H); **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 204.5, 174.9, 173.5, 152.6, 135.1, 134.9, 132.7, 129.0, 128.8, 128.7, 127.8, 122.5, 118.3, 107.6, 66.0, 55.1, 51.4, 35.4, 18.6, 18.5, 14.2; **HRMS** (APCI) calcd for $C_{28}H_{38}NOSSi$ $[MH]^+$: 464.2452, found: 464.2438 (3.0 ppm); ν_{max} (thin film)/cm^{-1}: 2944, 2865, 1713, 1490, 1462, 742.

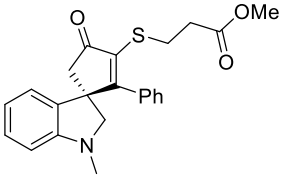
1'-Methyl-3-((2-methylbenzyl)thio)-2-phenylspiro[cyclopentane-1,3'-indolin]-2-en-4-one, 19o



Synthesised using **general procedure D** with 2-methylbenzyl mercaptan (44.0 µL, 0.32 mmol), ynone **13k** (54.6 mg, 0.2 mmol) and DCE (2.0 mL). Purification by column chromatography (hexane:EtOAc, 7:3 *v/v*) afforded the *title compound* **19o** (72.0 mg, 87%) as a yellow solid. Mp:159–160 °C; R_f = 0.40 (hexane:EtOAc, 7:3 *v/v*).

^1H NMR (400 MHz, $CDCl_3$) δ 7.25–7.01 (m, 9H), 6.66–6.61 (m, 3H), 6.54 (d, *J* = 7.4 Hz, 1H), 6.40 (d, *J* = 7.8 Hz, 1H), 4.18 (d, *J* = 12.9 Hz, 1H), 4.13 (d, *J* = 12.9 Hz, 1H), 3.30 (d, *J* = 9.6 Hz, 1H), 3.24 (d, *J* = 9.6 Hz, 1H), 2.85 (s, 2H), 2.58 (s, 3H), 2.19 (s, 3H); **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 204.5, 175.7, 152.3, 137.3, 135.4, 135.0, 134.1, 132.3, 130.6, 129.9, 128.9, 128.3, 127.7, 127.4, 125.7, 122.5, 118.3, 107.5, 65.5, 54.8, 52.0, 35.4, 33.9, 19.0; **HRMS** (ESI^+) calcd for $C_{27}H_{25}NNaOS$ $[MNa]^+$: 434.1549, found: 434.1549 (0.1 ppm error); ν_{max} (thin film)/cm^{-1}: 1705, 1604, 1490, 742, 730, 697.

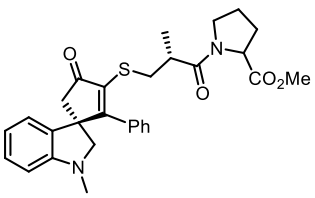
Methyl-3-((1'-methyl-4-oxo-2-phenylspiro[cyclopentane-1,3'-indolin]-2-en-3-yl)thio)propanoate, 19p



Synthesised using **general procedure D** with methyl 3-mercaptopropionate (35.0 µL, 0.32 mmol), ynone **13k** (54.6 mg, 0.2 mmol) and DCE (2.0 mL). Purification by column chromatography (hexane:EtOAc, 7:3 *v/v*) afforded the *title compound* **19p** (40.0 mg, 51%) as orange oil; R_f = 0.30 (hexane:EtOAc, 7:3 *v/v*).

^1H NMR (400 MHz, $CDCl_3$) δ 7.28–7.18 (m, 3H), 7.13 (td, *J* = 7.9, 1.3 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.94-6.91 (m, 2H), 6.42 (d, *J* = 8.1 Hz, 1H), 3.56 (s, 3H), 3.38 (d, *J* = 9.5 Hz, 1H), 3.28 (d, *J* = 9.5 Hz, 1H), 3.19 (dt, *J* = 13.6, 7.2 Hz, 1H), 3.05 (dt, *J* = 13.6, 7.2Hz, 1H), 2.90 (d, *J* = 19.0 Hz, 1H), 2.85 (d, *J* = 19.0 Hz, 1H), 2.59 (s, 3H), 2.56-2.50 (m, 2H); **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 204.1, 173.1, 172.0, 152.4, 134.8, 134.1, 132.5, 129.2, 129.1, 128.4, 128.0, 122.3, 118.5, 107.7, 65.6, 54.8, 52.3, 51.7, 35.4, 35.1, 26.1; **HRMS** (ESI^+) calcd for $C_{23}H_{24}NO_3S$ $[MH]^+$: 394.1471, found: 394.1469 (0.7 ppm); ν_{max} (thin film)/cm^{-1}:1735, 1706, 1603, 1245, 744, 699.

Methyl ((2R)-2-methyl-3-((1'-methyl-4-oxo-2-phenylspiro[cyclopentane-1,3'-indolin]-2-en-3-yl)thio)propanoyl)prolinate, 19q

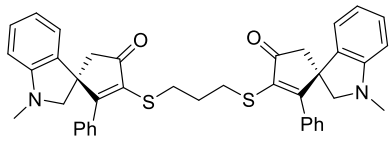


Synthesised using **general procedure D** with **SM5** (50.8 mg, 0.22 mmol), ynone **13k** (54.6 mg, 0.2 mmol) and DCE (2 mL). Purification by column chromatography (Fuji Silysia MB100-75/200, hexane:EtOAc, 3:1→ 1:1 *v/v*) afforded the *title compound* **19q** as 1:1 mixture of diastereoisomers (78.5 mg, 78%) as yellow oil; R_f = 0.25 (hexane:EtOAc, 1:1 *v/v*).

^1H NMR (400 MHz, $CDCl_3$) δ 7.45–7.22 (m, 10H), 7.14–7.10 (m, 4H), 6.90 (td, *J* = 7.7, 1.2 Hz, 1H), 6.87 (td, *J* = 7.7, 1.2 Hz, 1H), 6.62 (s, 1H), 6.61 (s, 1H), 4.56–4.48 (m, 2H), 3.85 (s, 3H), 3.82 (s, 3H), 3.71–3.63 (m, 4H), 3.56 (d, *J* = 9.5 Hz, 1H), 3.54 (d, *J* = 9.5 Hz, 1H), 3.47 (d, *J* = 9.5 Hz, 1H), 3.44 (d, *J* = 9.5 Hz, 1H), 3.26–3.17 (m, 2H), 3.05-2.86 (m, 8H), 2.78 (s, 3H), 2.77 (s, 3H), 2.26–1.89 (m, 8H), 1.29 (d, *J* = 6.8

Hz, 3H), 1.23 (d, *J* = 6.8 Hz, 3H); **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ 204.30, 204.26, 173.54, 173.50, 172.79, 172.74, 172.65, 172.31, 152.44, 152.39, 135.95, 135.60, 134.20, 134.10, 132.70, 132.68, 129.22, 129.16, 129.12, 129.06, 128.62, 128.57, 127.9 (2xC), 122.51, 122.14, 118.55, 118.38, 107.65, 107.62, 65.82, 65.62, 58.54, 58.46, 54.64, 54.59, 52.50, 52.34, 52.11 (2xC), 46.84, 46.75, 39.66, 39.47, 35.40, 35.34, 34.69, 34.56, 29.03, 28.94, 24.70, 24.63, 16.97, 16.74; **HRMS** (APCI$^+$) calcd for $C_{29}H_{33}N_2O_4S$ $[MH]^+$: 505.2162, found: 505.2156 (1.7 ppm); **ν_{max}** (thin film)/cm^{-1}: 2926, 1742, 1707, 1641, 1434, 1198, 1174, 731, 699.

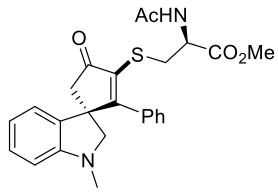
3,3''-(Propane-1,3-diylbis(sulfanediyl))bis(1'-methyl-2-phenylspiro[cyclopentane-1,3'-indolin]-2-en-4-one), 19r



Synthesised using **general procedure D** with 1,3-propanedithiol (10.0 µL, 0.1 mmol), ynone **13k** (54.6 mg, 0.2 mmol) and DCE (2.0 mL). Purification by column chromatography (hexane:EtOAc, 7:3 *v/v*) afforded the *title compound* **19r** (34.0 mg, 52%) as a yellow solid. Mp: 69–71 °C; R_f = 0.30 (hexane:EtOAc, 7:3 *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.20 (m, 6H), 7.14 (*app* t, *J* = 7.6 Hz, 2H), 6.93 (*app* t, *J* = 7.0 Hz, 6H), 6.69 (*app* t, *J* = 7.4 Hz, 2H), 6.44 (d, *J* = 7.9 Hz, 2H), 3.39 (d, *J* = 9.5 Hz, 2H), 3.29 (d, *J* = 9.5 Hz, 2H), 2.90–2.82 (m, 6H), 2.78–2.72 (m, 2H), 2.61 (s, 6H), 1.71–1.60 (m, 2H); **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ 204.2 (2xC), 173.0, 172.9, 152.4 (2xC), 135.0 (2xC), 134.2 (2xC), 132.5 (2xC), 129.1 (2xC), 129.0 (2xC), 128.3 (2xC), 128.0 (2xC), 122.3 (2xC), 118.6 (2xC), 107.6 (2xC), 65.6 (2xC), 54.8 (2xC), 52.2 (2xC), 35.4 (2xC), 30.0, 29.9, 29.3 (2xC); **HRMS** (ESI$^+$) calcd for $C_{41}H_{39}N_2O_2S_2$ $[MH]^+$: 655.2447, found: 655.2443 (0.7 ppm error); **ν_{max}** (thin film)/cm^{-1}: 1706, 1603, 1490, 742, 698.

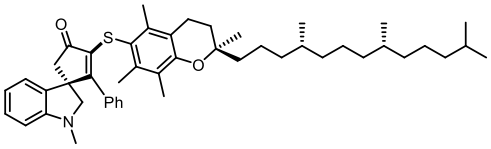
Methyl N-acetyl-S-(1'-methyl-4-oxo-2-phenylspiro[cyclopentane-1,3'-indolin]-2-en-3-yl)-D-cysteinate, 19s



Synthesised using **general procedure D** with **SM9** (56.7 mg, 0.32 mmol), ynone **13k** (54.6 mg, 0.2 mmol) and DCE (2.0 mL). Purification by column chromatography (hexane:EtOAc, 3:1 → 1:1 *v/v*) afforded the *title compound* **19s** as an inseparable 1:1 mixture of diastereoisomers (70.0 mg, 76%), as yellow oil; R_f = 0.16 (hexane:EtOAc, 1:1, *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.05 (m, 3H), 6.97 (*app* t, *J* = 7.8 Hz, 1H), 6.86 (dd, *J* = 7.4, 1.1 Hz, 0.5H), 6.81 (dd, *J* = 7.4, 1.1 Hz, 0.5H), 6.79–6.76 (m, 2H), 6.66 (d, *J* = 7.8 Hz, 1H), 6.56 (td, *J* = 7.8, 2.3 Hz, 1H) 6.26 (d, *J* = 7.8 Hz, 1H), 4.52–4.44 (m, 2H), 3.51 (s, 1.5 H), 3.47 (s, 1.5 H), 3.27–3.12 (m, 3H), 3.05 (dd, *J* = 14.2, 5.1 Hz, 0.5H), 2.99 (dd, *J* = 14.2, 5.1 Hz, 1H), 2.77 (dd, *J* = 18.7, 2.5 Hz, 1H), 2.70 (dd, *J* = 18.7, 2.5 Hz, 1H), 2.43 (s, 3H), 1.83 (s, 1.5 H), 1.79 (s, 1.5H); **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ 204.58, 204.51, 175.69, 175.60, 170.99, 170.05, 152.44, 152.39, 134.19, 134.12, 133.85 (2xC), 131.90, 131.84, 129.39, 129.35, 129.20, 129.18, 128.27 (2xC), 128.01 (2xC), 122.43, 122.36, 118.59 (2xC), 107.69 (2xC), 65.54, 65.46, 54.85, 54.78, 52.56, 52.51, 52.00, 51.95, 51.82 (2xC), 35.34 (2xC), 33.45, 33.32, 22.95, 22.92; **HRMS** (ESI$^+$) calcd for $C_{25}H_{27}N_2NaO_4S$ $[MNa]^+$: 473.1505, found: 473.1505 (0.1 ppm); **ν_{max}** (thin film)/cm^{-1}: 1703, 1665, 1212, 908, 726, 697.

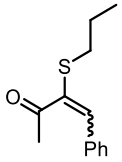
1'-Methyl-2-phenyl-3-(((R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl)thio)spiro[cyclopentane-1,3'-indolin]-2-en-4-one, 19t



Synthesised using general procedure C with **SM4** (147.33 mg, 0.33 mmol), ynone **13k** (81.9 mg, 0.3 mmol) and DCE (3.0 mL). Purification by column chromatography (hexane:EtOAc, 10:1→7:1 *v/v*) afforded the *title compound* **19t** as 1:1 mixture of diastereoisomers (156.7 mg, 74%) as a yellow oil; R_f = 0.23 (hexane:EtOAc, 10:1 *v/v*);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (td, *J* = 7.6, 1.7 Hz, 1H), 7.04 (d, *J* = 7.0 Hz, 1H), 7.01–6.98 (m, 1H), 6.93–6.88 (m, 2H), 6.75 (t, *J* = 7.6 Hz, 1H), 6.59–6.55 (m, 2H), 6.31 (d, *J* = 7.6 Hz, 1H), 3.33 (d, *J* = 9.0 Hz, 1H), 3.28 (d, *J* = 9.0 Hz, 1H), 2.92 (app d, *J* = 19.0 Hz, 1H), 2.86 (d, 19,0 Hz, 1H), 2.54 (s, 3H), 2.45–2.34 (m ,2H), 2.29 (d, J = 3.3 Hz, 3H), 1.93 (d, J = 4.6 Hz, 3H), 1.67–1.06 (m, 26H), 0.89–0.84 (m, 12H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 204.09, 204.05, 167.13, 167.06, 152.56 (2xC), 152.13 (2xC), 139.03, 139.00, 138.22, 138.18, 137.20, 137.17, 133.48, 133.46, 132.75(2xC), 128.82 (2XC), 127.68, 127.64, 127.19, 127.15, 126.61, 126.59, 122.80 (2xC), 122.35 (2xC), 118.28, 118.23, 118.15 (2xC), 117.21(2xC), 107.45 (2xC), 75.10 (2xC), 65.47, 65.46, 55.19, 55.18, 51.43 (2xC), 40.44, 40.40, 40.07, 40.01, 39.34 (2xC), 37.55, 37.42, 37.36, 37.26, 35.25 (2xC), 32.76, 32.70, 31.06, 31.03, 31.02, 30.96, 27.95 (2xC), 24.79, 24.42, 24.00, 23.72, 22.70, 22.61, 21.10, 21.01, 19.73, 19.66, 19.60, 19.57, 18.88 (2xC), 18.01 (2xC), 12.25 (2xC); **HRMS** (APCI$^+$) calcd for $C_{48}H_{66}NO_2S$ [MH]$^+$:720.4809, found: 720.4781 (3.9 ppm); $\mathbf{\nu_{max}}$ (thin film)/cm^{-1}: 2943, 2866, 1711, 1605, 1490, 1460, 1102, 742, 698.

4-Phenyl-3-(propylthio)but-3-en-2-one, 21 [12]

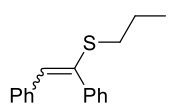


Synthesised using **general procedure D** with n-propane thiol (48.9 µL, 0.54 mmol), 4-phenylbut-3-yn-2-one **20** (43.3 mg, 0.3 mmol), ynone **13k** (16.4 mg, 0.06 mmol) and DCE (3.0 mL). Purification by column chromatography (hexane:EtOAc) afforded the *title compound* **21** as mixture of E/Z isomer (35.7 mg, 54%, *E/Z* = 43:57) as yellow oil; R_f = 0.30 (*E*-isomer) and R_f = 0.16 (*Z*-isomer) (hexane:EtOAc, 20:1 *v/v*).

^{1}H NMR for *E*-isomer (400 MHz, $CDCl_3$) δ 7.34-7.21 (m, 2H), 6.85 (s, 1H), 2.66 (*app* t, *J* = 7.3 Hz, 2H), 2.24 (s, 3H), 1.72–1.63 (m, 2H), 1.02 (t, *J* = 7.3 Hz, 3H); **^{13}C{^{1}H} NMR** for *E*-isomer (100 MHz, $CDCl_3$) δ 202.8, 137.3, 135.3, 132.0, 128.6, 128.4, 128.2, 34.7, 29.9, 22.5, 13.3; **HRMS** (ESI) calcd for $C_{13}H_{17}OS$ [MH]$^+$: 221.0994, found: 221.0995 (0.3 ppm); $\mathbf{\nu_{max}}$ (thin film)/cm^{-1}: 2962, 2927, 1694, 1354, 1172, 757, 699;

^{1}H NMR for *Z*-isomer (400 MHz, $CDCl_3$) δ 7.86-7.83 (m, 2H), 7.64 (s, 1H), 7.43–7.34 (m, 3H), 2.67 (app t, *J* = 7.2 Hz, 2H), 2.55 (s, 3H), 1.56–1.47 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); **^{13}C{^{1}H} NMR** for *Z*-isomer (100 MHz, $CDCl_3$) δ 198.6, 141.6, 136.3, 134.7, 130.9, 129.5, 128.3, 35.9, 27.5, 23.2, 13.3; **HRMS** (ESI) calcd for $C_{13}H_{17}OS$ [MH]$^+$: 221.0995, found: 221.0995 (0.3 ppm); $\mathbf{\nu_{max}}$ (thin film)/cm^{-1}: 2963, 2929, 1677, 1204, 1219, 1181, 755, 691.

(1,2-Diphenylvinyl)(propyl)sulfane, 23



Prepared using general **procedure D** with n-propane thiol (32.6 µL, 0.36 mmol), diphenylacetylene **22** (35.7 mg, 0.2 mmol), ynone **13k** (10.9 mg, 0.04 mmol) and DCE (2.0 mL). Purification by column chromatography (hexane) afforded the *title compound* **23** as an inseparable mixture of E/Z isomers (40.7 mg, 80%, *E/Z* = 40:60), as yellow oil; R_f = 0.29 (hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.2 Hz, 2H), 7.63 (d, *J* = 7.8 Hz, 2H), 7.42-7.29 (m, 12H), 7.13–7.08 (m, 4H), 6.96 (d, *J* = 7.6 Hz, 2H), 6.83 (s, 1H, major), 6.17 (s, 1H, minor), 2.54 (t, *J* = 7.2 Hz, 2H, minor), 2.42 (t, *J* = 7.2 Hz, 2H, major), 1.68–1.69 (m, 2H, minor), 1.52–1.43 (m, 2H, major), 0.99 (t, *J* = 7.4 Hz, 3H,minor), 0.85 (t, *J* = 7.4 Hz, 3H, major) ;**^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 141.2, 138.3, 138.1, 137.8, 137.1, 136.8, 131.9, 129.6, 129.5, 128.8, 128.6, 128.3, 128.0, 127.9, 127.9(3), 127.8, 127.1, 126.6, 126.4, 34.8, 33.8, 23.2, 22.5, 13.4, 13.2; **HRMS** (APCI) calcd for $C_{17}H_{19}S$ $[MH]^+$: 255.1187, found: 255.1202 (5.7 ppm); $\mathbf{\nu_{max}}$ (thin film)/cm^{-1}: 2961, 1444, 763, 692.

DFT Computational Analysis

All calculations were carried out using the ORCA 4.0.1 software package.[14] This work was performed on the Viking Cluster, which is a high-performance computer facility provided by the University of York. We are grateful for computational support from the University of York High Performance Computing service, Viking and the Research Computing team.

The ground state geometry of ynone **13k** was optimised using the B3LYP hybrid functional[15] with Ahlrich's def2-SVP double-zeta basis set.[16] The obtained geometry was confirmed to be a local minimum by frequency analysis at the same level. The optimized structure is given below in .xyz format and visualized using ChemCraft.[17] This ground state geometry was analysed by time-dependent density functional theory (TDDFT) at the B3LYP def2-TZVPP level. The first 10 excited states are reported below and the key contributing molecular orbitals (71 & 72) are depicted using ChemCraft.

To investigate the effect of ynone conformation we also optimised the geometry of ynone **13k** using the B3LYP hybrid functional with Grimme's D3 dispersion correction[18] Ahlrich's def2-SVP double-zeta basis set[15] and the SMD solvation model (DCE).[19] This geometry was analysed by TDDFT at the B3LYP-D3 def2-TZVPP level using the SMD solvation model (DCE). For both geometries, the lowest energy excited state was determined to be composed entirely of a charge transfer excitation between the π orbitals of the indole HOMO (MO 71) and ynone LUMO (MO 72).

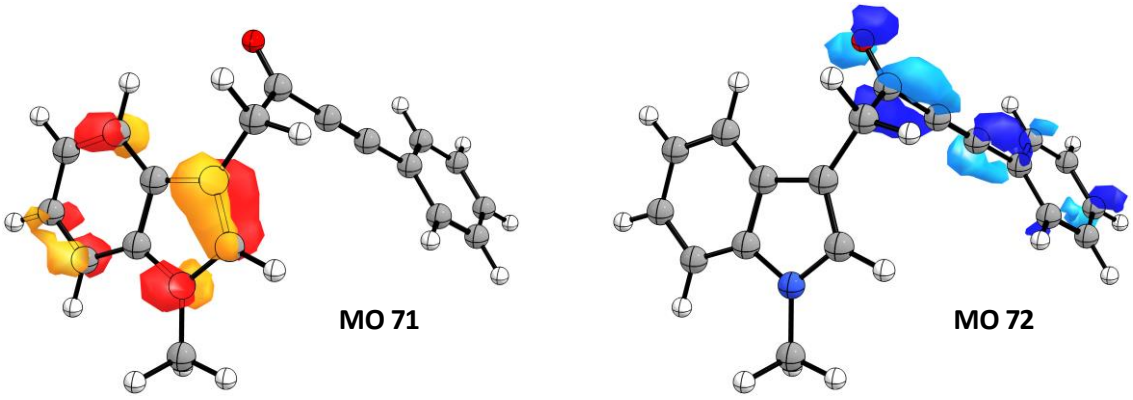
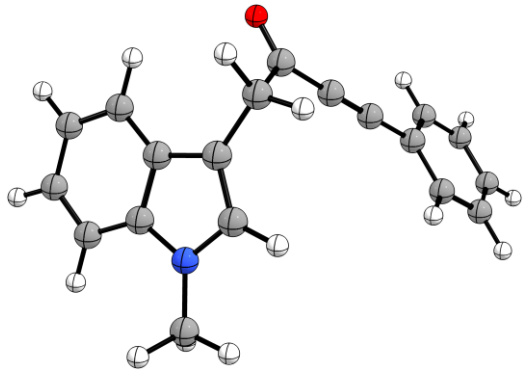


Figure 2. Calculated molecular orbitals 71 & 72 representing the π orbitals of the indole HOMO and ynone LUMO (isosurface contour values set at 0.072 a.u.).

Ynone 13k (Gas phase)



C	0.030711	0.363732	-2.838136
C	0.160596	-0.212847	-4.098798
C	-0.756767	-1.183858	-4.556629
C	-1.824081	-1.601081	-3.763835
C	-1.955175	-1.018860	-2.493997
C	-1.041043	-0.035264	-2.015689
H	0.754202	1.101528	-2.482118
H	0.988870	0.086070	-4.746748
H	-0.626638	-1.618743	-5.551068
H	-2.529737	-2.354036	-4.123512
N	-2.902128	-1.234673	-1.510670
C	-2.608752	-0.413879	-0.437649
C	-1.486341	0.342317	-0.694510
H	-3.241442	-0.423670	0.450009
C	-4.013450	-2.152547	-1.607535
H	-4.589422	-2.128592	-0.671959
H	-3.664707	-3.186562	-1.772112
H	-4.688661	-1.880523	-2.437444
C	-0.843784	1.350747	0.217465
C	0.549835	0.901477	0.665768
H	-1.476950	1.508040	1.105536
H	-0.707328	2.318386	-0.292520
O	1.565271	1.359958	0.178100
C	0.593877	-0.126773	1.693422
C	0.633219	-0.973167	2.571247
C	0.702938	-1.964359	3.597442
C	1.954774	-2.434575	4.051454
C	2.020885	-3.401861	5.053404
C	0.846915	-3.914470	5.616902
C	-0.399079	-3.456016	5.174266
C	-0.474940	-2.488787	4.172915
H	-1.444470	-2.127627	3.823589
H	-1.316691	-3.855443	5.613330
H	2.867008	-2.031052	3.607430
H	2.994504	-3.759275	5.397766
H	0.903502	-4.672576	6.402743

ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS

State	Energy (cm-1)	Wavelength (nm)	fosc	T2 (au**2)	TX (au)	TY (au)	TZ (au)
1	21205.5	471.6	0.000000000	0.00000	0.00000	0.00000	-0.00000
2	**22661.6**	**441.3**	**0.049959067**	**0.72577**	**0.43054**	**-0.04545**	**0.73371**
3	24882.7	401.9	0.000000000	0.00000	0.00000	-0.00000	0.00000
4	26706.8	374.4	0.000000000	0.00000	0.00000	-0.00000	0.00000
5	27348.0	365.7	0.000000006	0.00000	0.00020	-0.00004	0.00016
6	27557.8	362.9	0.000000000	0.00000	-0.00000	0.00000	-0.00000
7	27838.2	359.2	0.005914252	0.06994	-0.03075	-0.03175	-0.26074
8	30123.6	332.0	0.002214886	0.02421	0.05593	-0.08420	0.11827
9	32597.8	306.8	0.000001404	0.00001	0.00079	0.00285	-0.00234
10	32636.6	306.4	0.000000004	0.00000	-0.00004	-0.00016	0.00013

TD-DFT/TDA EXCITED STATES

STATE 1: E= 0.096619 au 2.629 eV 21205.5 cm**-1
68a -> 72a : 0.032709 (c= -0.18085695)
71a -> 72a : 0.433458 (c= 0.65837541)
71a -> 74a : 0.012205 (c= -0.11047752)
68b -> 72b : 0.032709 (c= 0.18085696)
71b -> 72b : 0.433458 (c= -0.65837541)
71b -> 74b : 0.012205 (c= 0.11047751)

STATE 2: E= 0.103254 au 2.810 eV 22661.6 cm-1**
71a -> 72a : 0.484864 (c= 0.69632149)
71b -> 72b : 0.484864 (c= 0.69632149)

STATE 3: E= 0.113374 au 3.085 eV 24882.7 cm**-1
68a -> 72a : 0.019675 (c= 0.14026820)
69a -> 72a : 0.439554 (c= -0.66298874)
68b -> 72b : 0.019675 (c= -0.14026819)
69b -> 72b : 0.439554 (c= 0.66298873)

STATE 4: E= 0.121685 au 3.311 eV 26706.8 cm**-1
66a -> 72a : 0.042865 (c= -0.20703936)

68a -> 72a : 0.214432 (c= -0.46306768)
68a -> 74a : 0.010982 (c= 0.10479294)
68a -> 75a : 0.013200 (c= -0.11488971)
71a -> 72a : 0.014387 (c= -0.11994510)
71a -> 74a : 0.135326 (c= 0.36786629)
71a -> 75a : 0.030118 (c= 0.17354681)
66b -> 72b : 0.042865 (c= 0.20703934)
68b -> 72b : 0.214432 (c= 0.46306769)
68b -> 74b : 0.010982 (c= -0.10479293)
68b -> 75b : 0.013200 (c= 0.11488971)
71b -> 72b : 0.014387 (c= 0.11994510)
71b -> 74b : 0.135326 (c= -0.36786631)
71b -> 75b : 0.030118 (c= -0.17354681)

STATE 5: E= 0.124607 au 3.391 eV 27348.0 cm**-1
66a -> 72a : 0.019310 (c= 0.13896218)
68a -> 72a : 0.072669 (c= 0.26957116)
68a -> 75a : 0.011267 (c= 0.10614573)
70a -> 72a : 0.165846 (c= 0.40724228)
71a -> 72a : 0.033734 (c= 0.18366899)
71a -> 74a : 0.151298 (c= 0.38897095)
71a -> 75a : 0.015115 (c= 0.12294127)
66b -> 72b : 0.019338 (c= -0.13906079)
68b -> 72b : 0.072649 (c= -0.26953495)
68b -> 75b : 0.011262 (c= -0.10612102)
70b -> 72b : 0.165857 (c= -0.40725551)
71b -> 72b : 0.033729 (c= -0.18365568)
71b -> 74b : 0.151512 (c= -0.38924510)
71b -> 75b : 0.015167 (c= -0.12315398)

STATE 6: E= 0.125563 au 3.417 eV 27557.8 cm**-1
68a -> 72a : 0.026926 (c= -0.16409208)
70a -> 72a : 0.317531 (c= 0.56349889)
71a -> 74a : 0.104369 (c= -0.32306260)
71a -> 75a : 0.012311 (c= -0.11095687)
68b -> 72b : 0.026926 (c= 0.16409212)
70b -> 72b : 0.317531 (c= -0.56349889)
71b -> 74b : 0.104369 (c= 0.32306266)
71b -> 75b : 0.012311 (c= 0.11095678)

STATE 7: E= 0.126840 au 3.451 eV 27838.2 cm**-1

70a -> 72a : 0.496269 (c= -0.70446342)

70b -> 72b : 0.496269 (c= -0.70446342)

STATE 8: E= 0.137253 au 3.735 eV 30123.6 cm**-1

66a -> 72a : 0.058771 (c= 0.24242668)

68a -> 72a : 0.393653 (c= 0.62741761)

68a -> 75a : 0.020110 (c= 0.14181044)

71a -> 72a : 0.010010 (c= 0.10005161)

66b -> 72b : 0.058771 (c= 0.24242652)

68b -> 72b : 0.393653 (c= 0.62741763)

68b -> 75b : 0.020110 (c= 0.14181048)

71b -> 72b : 0.010010 (c= 0.10005162)

STATE 9: E= 0.148527 au 4.042 eV 32597.8 cm**-1

70a -> 74a : 0.386379 (c= 0.62159403)

70a -> 75a : 0.061254 (c= 0.24749569)

70b -> 74b : 0.386496 (c= -0.62168805)

70b -> 75b : 0.061247 (c= -0.24748207)

STATE 10: E= 0.148703 au 4.046 eV 32636.6 cm**-1

67a -> 72a : 0.424474 (c= 0.65151705)

67a -> 74a : 0.010134 (c= 0.10066962)

67a -> 75a : 0.020269 (c= -0.14236772)

69a -> 73a : 0.030971 (c= -0.17598686)

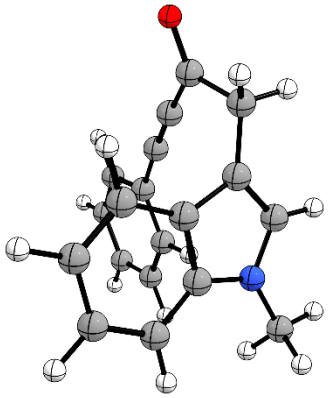
67b -> 72b : 0.424476 (c= -0.65151827)

67b -> 74b : 0.010134 (c= -0.10066865)

67b -> 75b : 0.020268 (c= 0.14236738)

69b -> 73b : 0.030971 (c= 0.17598535)

Ynone 13k (*in DCE*)



C	0.210323	-0.050366	-2.252494
C	0.535717	-1.137779	-3.061370
C	-0.256904	-2.308259	-3.064614
C	-1.388264	-2.419317	-2.256628
C	-1.709365	-1.326762	-1.437758
C	-0.928600	-0.130596	-1.429002
H	0.832069	0.849303	-2.257491
H	1.418719	-1.088725	-3.704030
H	0.023446	-3.144281	-3.710882
H	-1.995878	-3.326996	-2.260245
N	-2.737018	-1.166694	-0.529299
C	-2.631185	0.090228	0.036672
C	-1.543075	0.763183	-0.477865
H	-3.346769	0.410139	0.793398
C	-3.795019	-2.125229	-0.286404
H	-4.396194	-1.790882	0.569462
H	-3.376496	-3.116315	-0.050097
H	-4.454777	-2.227231	-1.164392
C	-1.003585	2.084780	-0.029286
C	0.300669	1.995564	0.770834
H	-1.729610	2.584143	0.637274
H	-0.809395	2.778587	-0.863579
O	1.117444	2.899615	0.782379
C	0.478812	0.767211	1.517642
C	0.543520	-0.331097	2.044189
C	0.539217	-1.647806	2.588002
C	1.514761	-2.065807	3.517273
C	1.484182	-3.365625	4.021276
C	0.490421	-4.259871	3.605377
C	-0.480681	-3.852959	2.681797
C	-0.462502	-2.555344	2.174703
H	-1.214967	-2.224988	1.455945
H	-1.255229	-4.552199	2.357500
H	2.288625	-1.364024	3.834558
H	2.240699	-3.684795	4.742418
H	0.472409	-5.277665	4.002600

ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS

State	Energy (cm-1)	Wavelength (nm)	fosc	T2 (au**2)	TX (au)	TY (au)	TZ (au)
1	18024.8	554.8	0.000000000	0.00000	0.00000	-0.00000	0.00000
2	**17997.5**	**555.6**	**0.000772766**	**0.01414**	**-0.10794**	**-0.00616**	**-0.04946**
3	24353.8	410.6	0.000000000	0.00000	-0.00000	0.00000	-0.00000
4	26681.9	374.8	0.000000000	0.00000	-0.00000	-0.00000	0.00000
5	22596.1	442.6	0.000000000	0.00000	0.00000	-0.00001	0.00001
6	22046.6	453.6	0.005280567	0.07885	0.09247	-0.03581	0.26272
7	27081.6	369.3	0.000000000	0.00000	-0.00000	-0.00000	0.00000
8	30142.3	331.8	0.000567622	0.00620	0.01392	-0.07343	-0.02477
9	29831.5	335.2	0.000000001	0.00000	0.00002	-0.00007	0.00005
10	32132.5	311.2	0.000000050	0.00000	-0.00005	0.00042	-0.00058

TD-DFT/TDA EXCITED STATES

STATE 1: E= 0.082127 au 2.235 eV 18024.8 cm**-1
68a -> 72a : 0.018853 (c= -0.13730443)
71a -> 72a : 0.466278 (c= -0.68284532)
68b -> 72b : 0.018853 (c= 0.13730443)
71b -> 72b : 0.466278 (c= 0.68284532)

STATE 2: E= 0.082003 au 2.231 eV 17997.5 cm-1**
71a -> 72a : 0.491122 (c= 0.70080108)
71b -> 72b : 0.491122 (c= 0.70080111)

STATE 3: E= 0.110964 au 3.019 eV 24353.8 cm**-1
69a -> 72a : 0.440107 (c= -0.66340534)
70a -> 72a : 0.022954 (c= -0.15150656)
69b -> 72b : 0.440106 (c= 0.66340488)
70b -> 72b : 0.022954 (c= 0.15150655)

STATE 4: E= 0.121572 au 3.308 eV 26681.9 cm**-1
70a -> 72a : 0.011815 (c= 0.10869545)

71a -> 73a : 0.279378 (c= -0.52856233)
71a -> 74a : 0.161766 (c= 0.40220203)
70b -> 72b : 0.011815 (c= -0.10869544)
71b -> 73b : 0.279378 (c= 0.52856216)
71b -> 74b : 0.161766 (c= -0.40220194)

STATE 5: E= 0.102955 au 2.802 eV 22596.1 cm**-1
69a -> 72a : 0.021050 (c= 0.14508669)
70a -> 72a : 0.460347 (c= -0.67848873)
69b -> 72b : 0.021049 (c= -0.14508436)
70b -> 72b : 0.460347 (c= 0.67848850)

STATE 6: E= 0.100452 au 2.733 eV 22046.6 cm**-1
70a -> 72a : 0.498388 (c= 0.70596585)
70b -> 72b : 0.498387 (c= 0.70596501)

STATE 7: E= 0.123393 au 3.358 eV 27081.6 cm**-1
66a -> 72a : 0.108290 (c= 0.32907390)
66a -> 75a : 0.012862 (c= 0.11341043)
67a -> 72a : 0.026965 (c= -0.16420958)
68a -> 72a : 0.279472 (c= -0.52865111)
68a -> 75a : 0.021575 (c= -0.14688403)
71a -> 72a : 0.029769 (c= 0.17253611)
66b -> 72b : 0.108289 (c= -0.32907365)
66b -> 75b : 0.012862 (c= -0.11341043)
67b -> 72b : 0.026965 (c= 0.16420984)
68b -> 72b : 0.279472 (c= 0.52865125)
68b -> 75b : 0.021575 (c= 0.14688395)
71b -> 72b : 0.029769 (c= -0.17253610)

STATE 8: E= 0.137339 au 3.737 eV 30142.3 cm**-1
66a -> 72a : 0.079575 (c= -0.28209093)
67a -> 72a : 0.031966 (c= 0.17879167)
68a -> 72a : 0.346122 (c= 0.58832170)
68a -> 75a : 0.013949 (c= 0.11810781)
66b -> 72b : 0.079604 (c= -0.28214195)
67b -> 72b : 0.031977 (c= 0.17882038)
68b -> 72b : 0.346069 (c= 0.58827634)
68b -> 75b : 0.013953 (c= 0.11812302)

STATE 9: E= 0.135922 au 3.699 eV 29831.5 cm**-1

67a -> 72a : 0.414108 (c= -0.64351188)

67a -> 75a : 0.026120 (c= 0.16161545)

68a -> 72a : 0.039384 (c= 0.19845427)

67b -> 72b : 0.414108 (c= 0.64351220)

67b -> 75b : 0.026120 (c= -0.16161552)

68b -> 72b : 0.039384 (c= -0.19845318)

STATE 10: E= 0.146407 au 3.984 eV 32132.5 cm**-1

70a -> 73a : 0.293285 (c= 0.54155790)

70a -> 74a : 0.176208 (c= -0.41977131)

70b -> 73b : 0.293252 (c= -0.54152786)

70b -> 74b : 0.176147 (c= 0.41969848)

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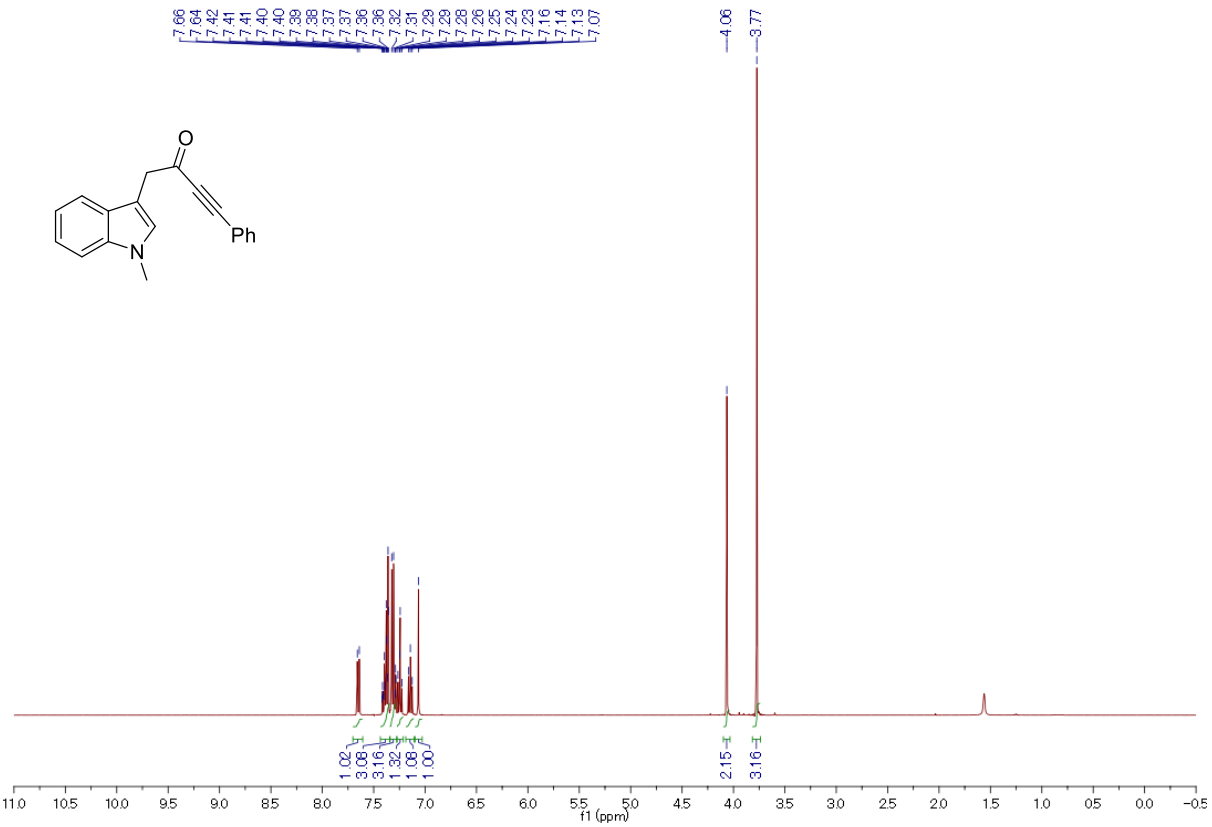
7.66
7.64
7.42
7.41
7.41
7.40
7.40
7.39
7.38
7.37
7.37
7.36
7.36
7.32
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7.26
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7.24
7.23
7.16
7.14
7.13
7.07
4.06
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3.16
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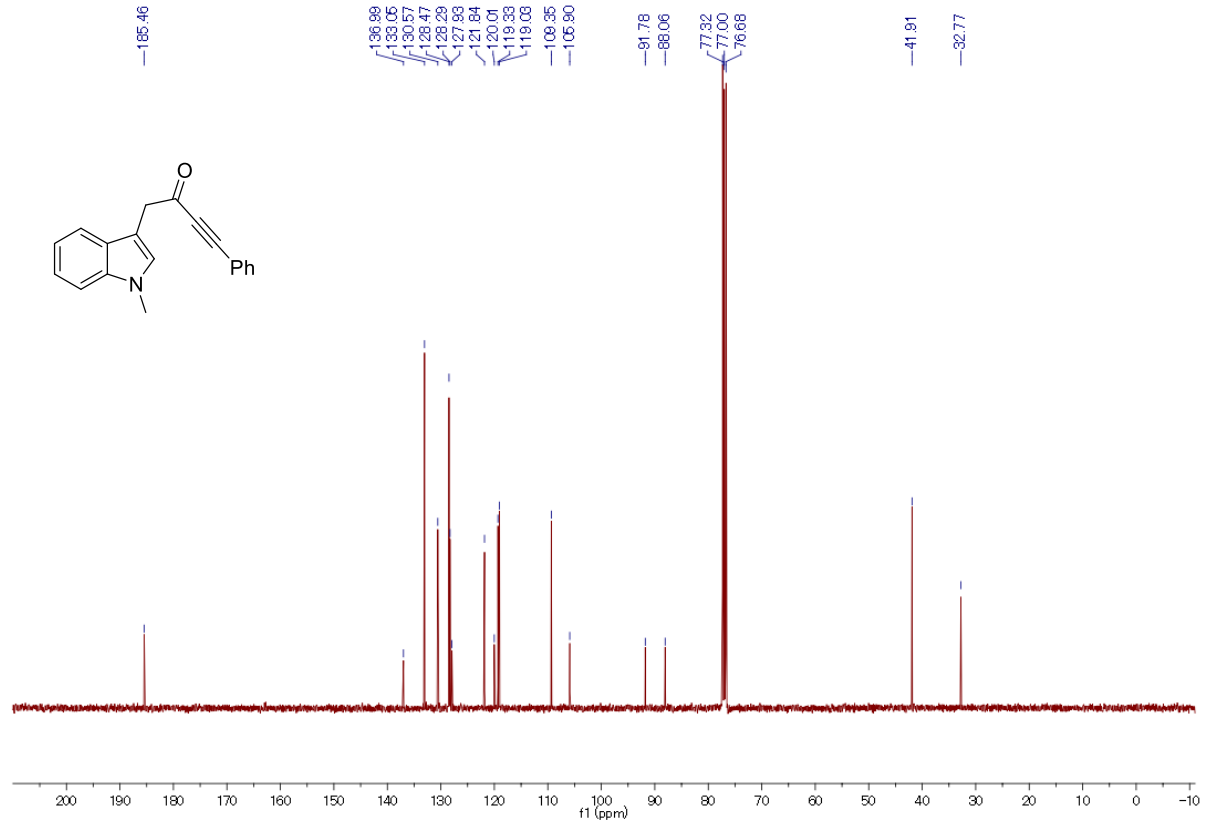
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77.00
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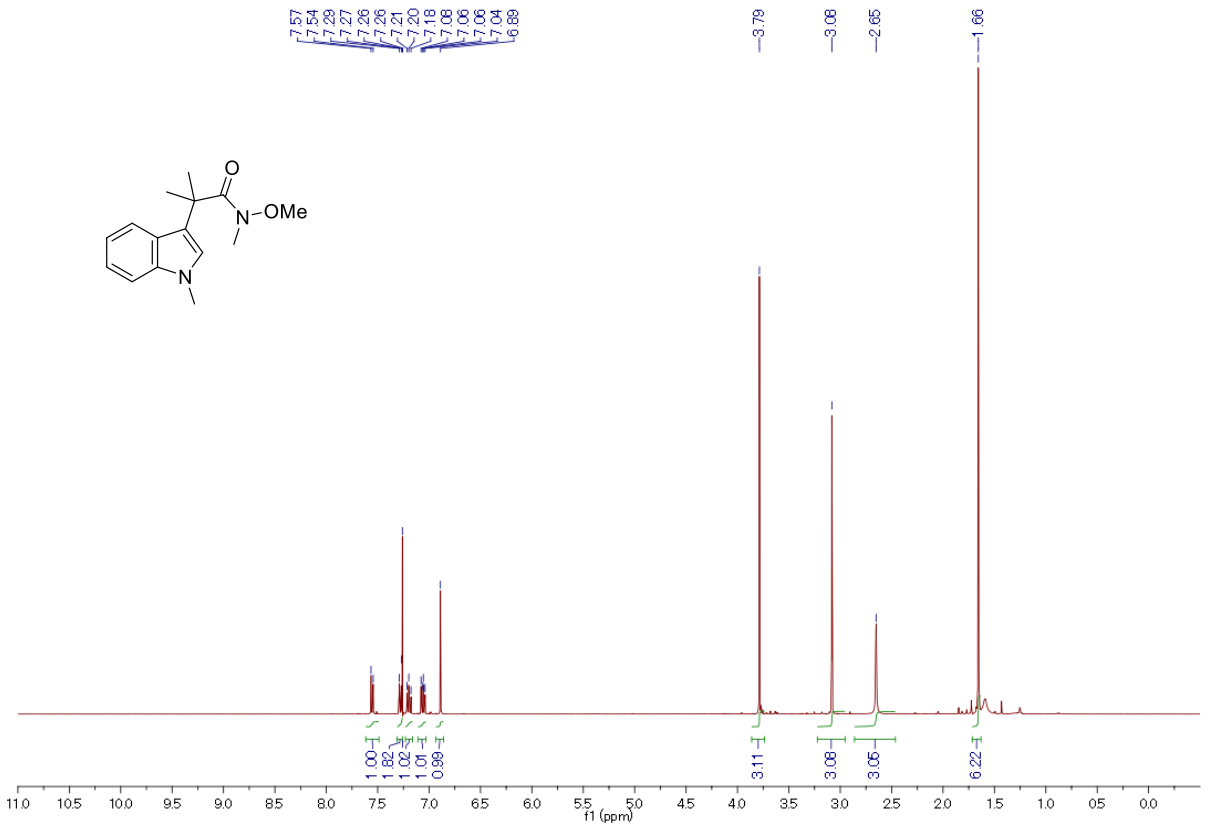
41.91
32.77
O
Ph
N
f1 (ppm)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3.06
2.65
1.66
O
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1.01
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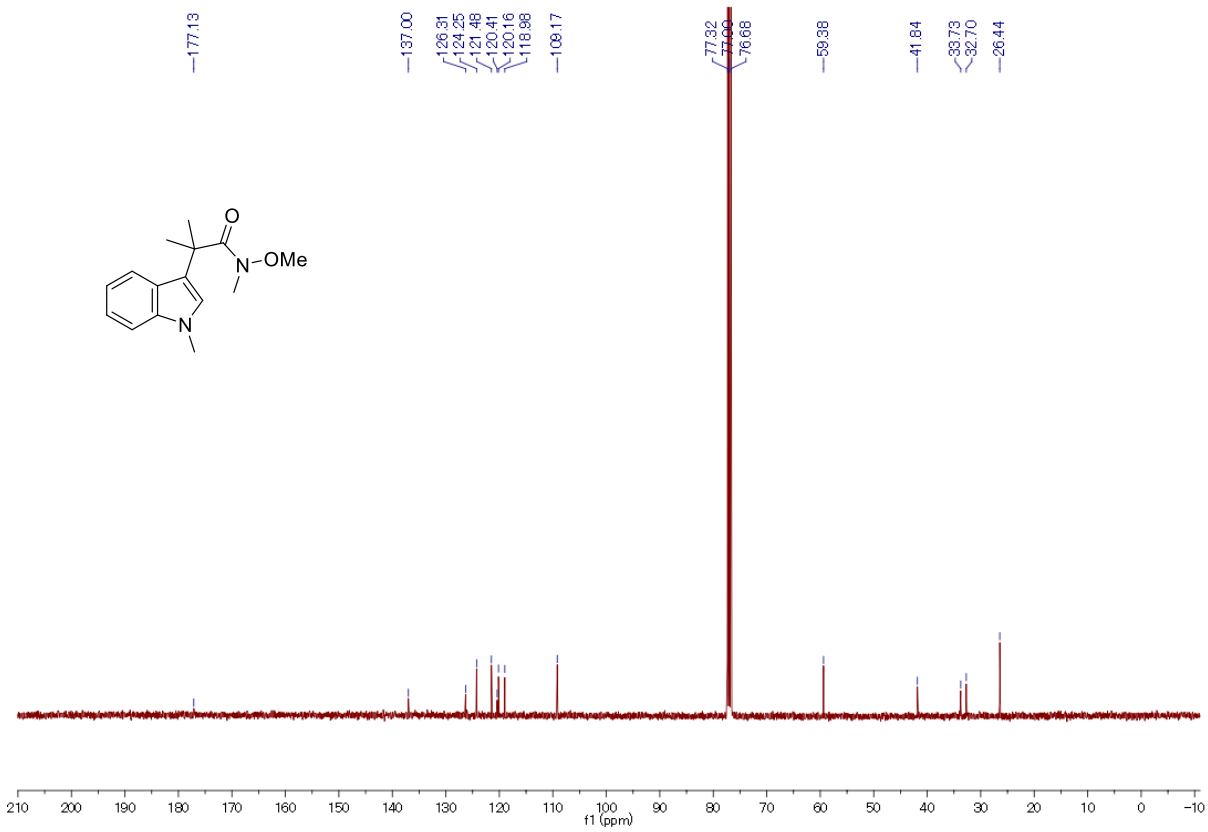
3.08
3.05
6.22
f1 (ppm)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33.73
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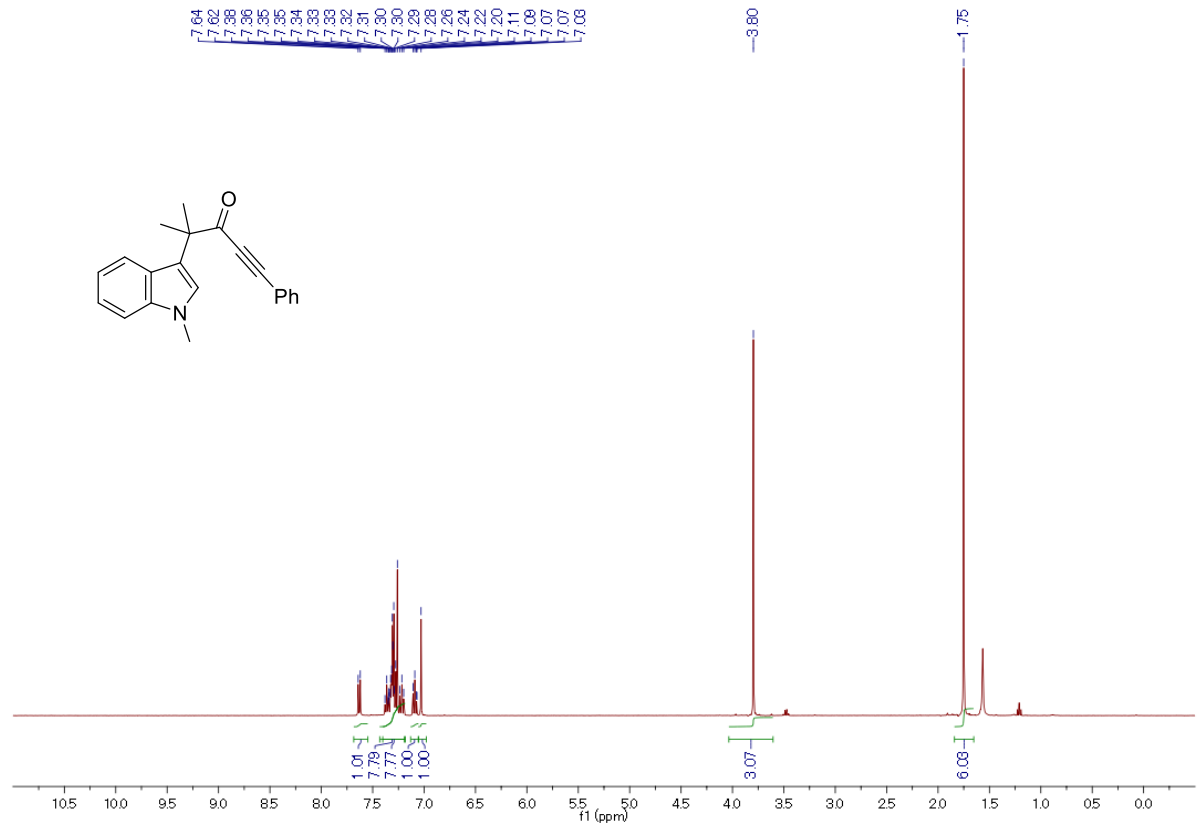
26.44
O
N-OMe
N
f1 (ppm)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7.24
7.22
7.20
7.11
7.08
7.07
7.07
7.03
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7.79
7.77
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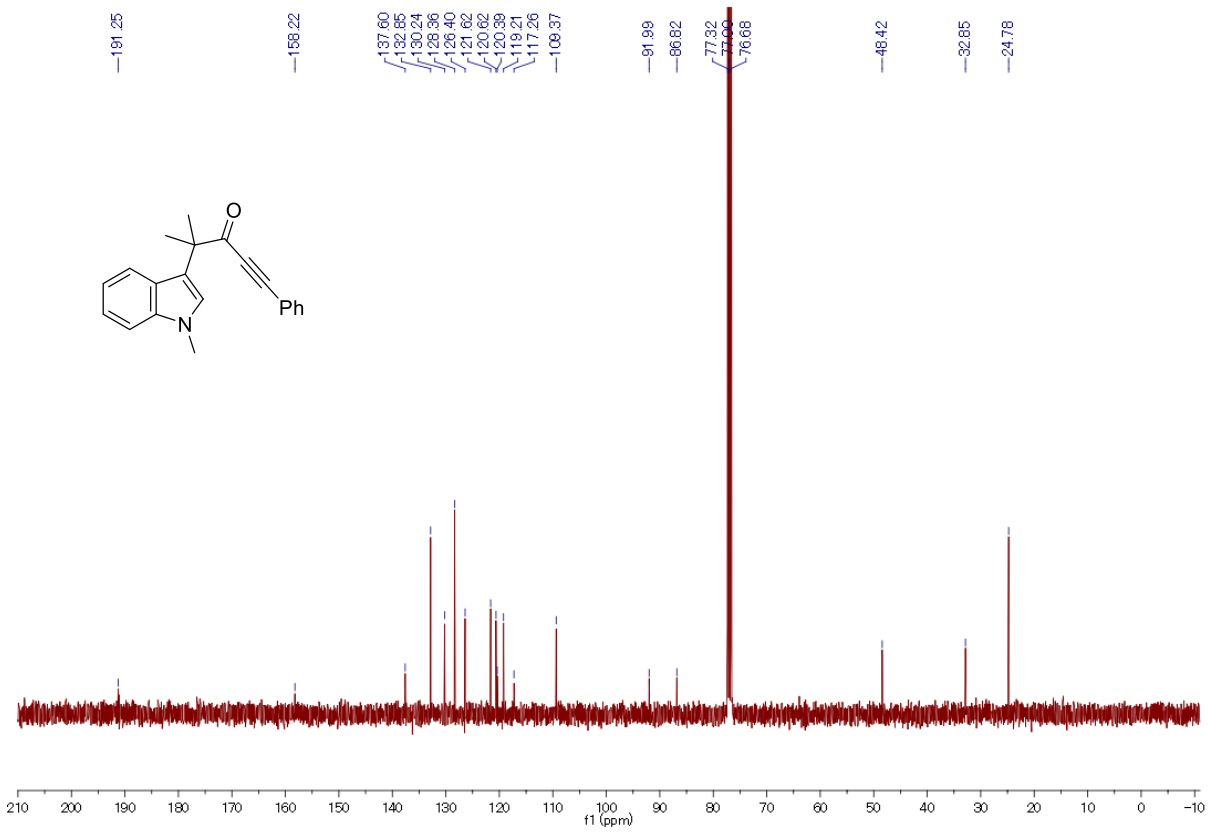
1.00
3.07
6.03
f1 (ppm)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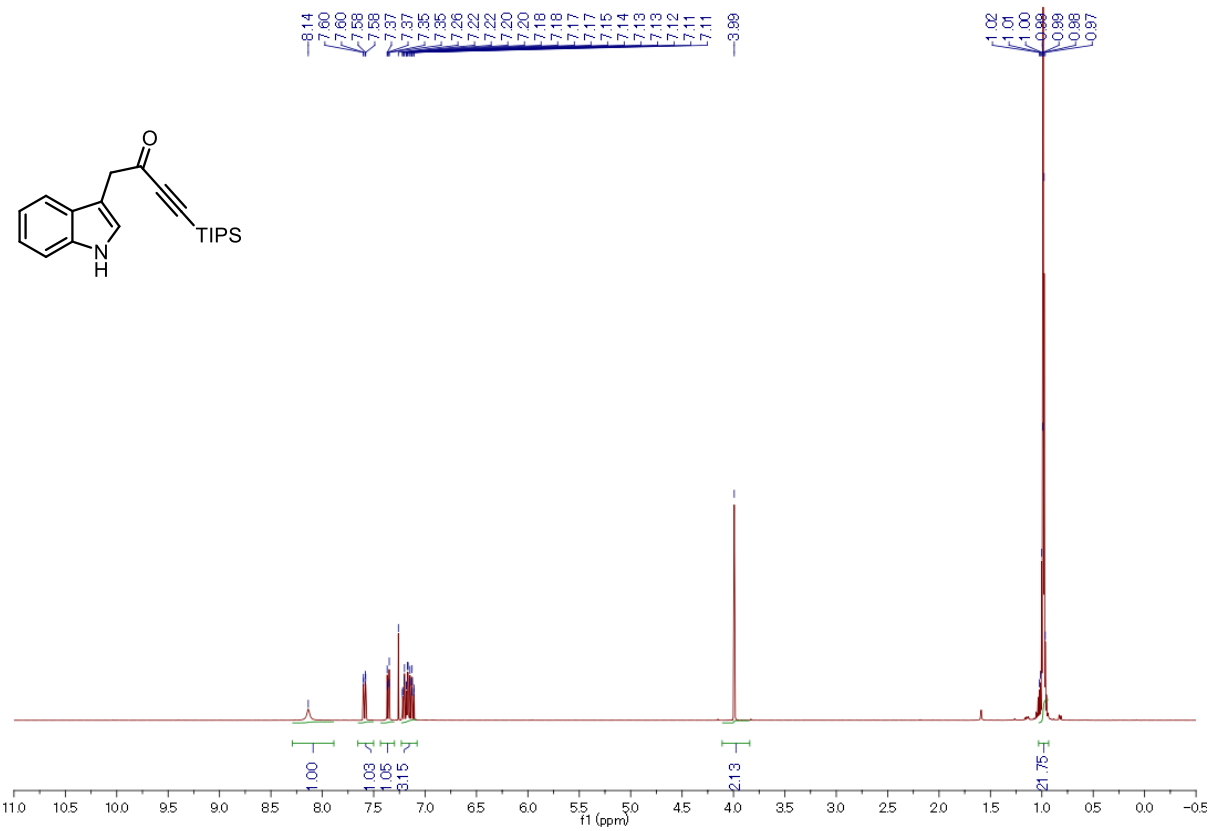
32.85
24.78
O
Ph
N
f1 (ppm)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7.18
7.18
7.17
7.17
7.15
7.14
7.13
7.13
7.12
7.11
7.11
3.99
1.02
1.01
1.00
0.99
0.99
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TIPS
N
H
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1.03
1.05
3.15
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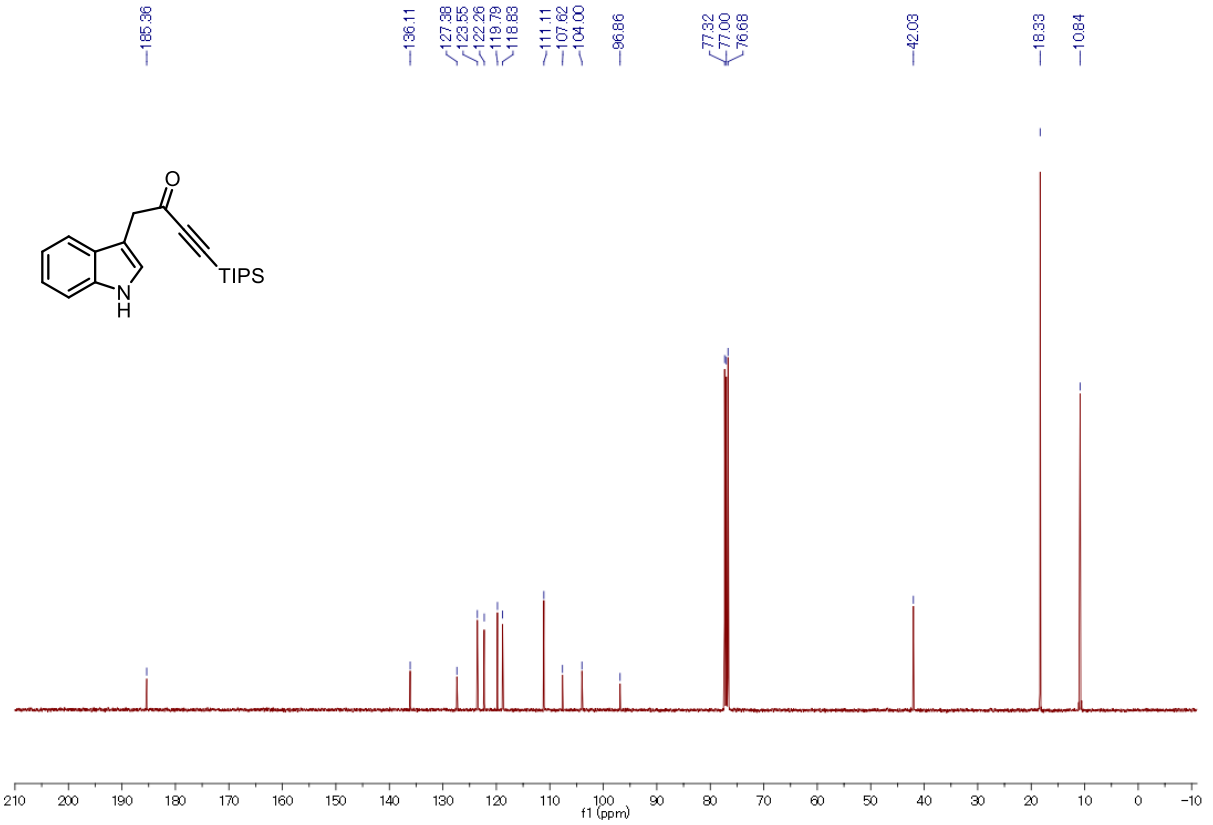
21.75
f1 (ppm)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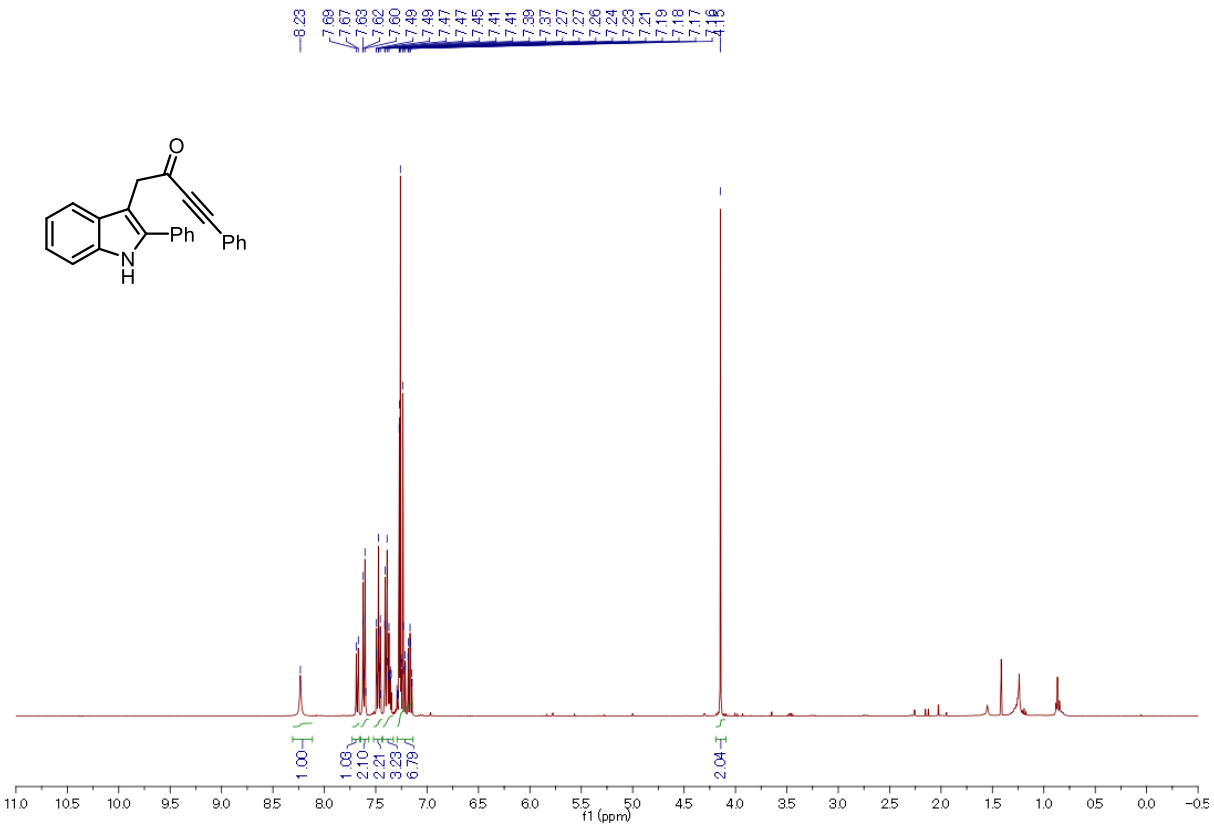
10.84
O
TIPS
N
H
f1 (ppm)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7.39
7.37
7.27
7.27
7.26
7.24
7.23
7.21
7.19
7.18
7.17
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N
H
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1.03
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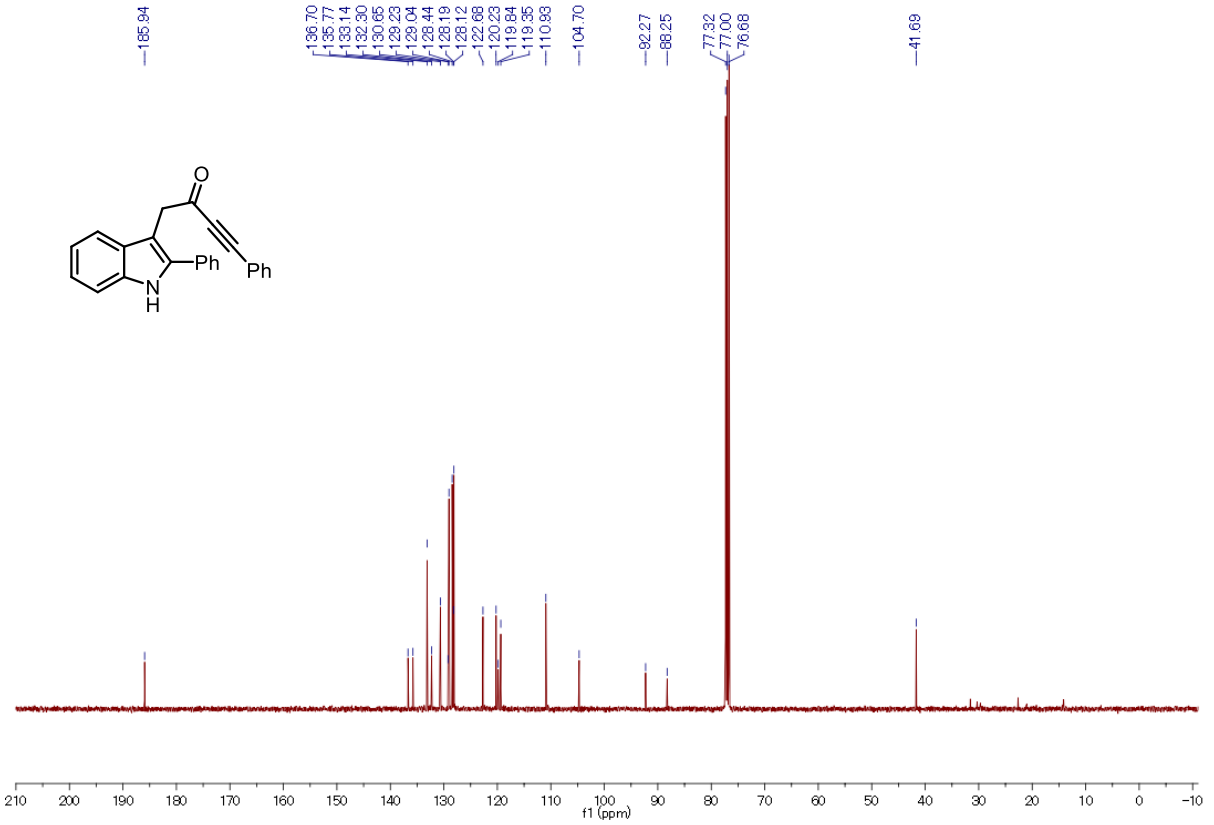
2.21
3.23
6.79
2.04
f1 (ppm)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129.04
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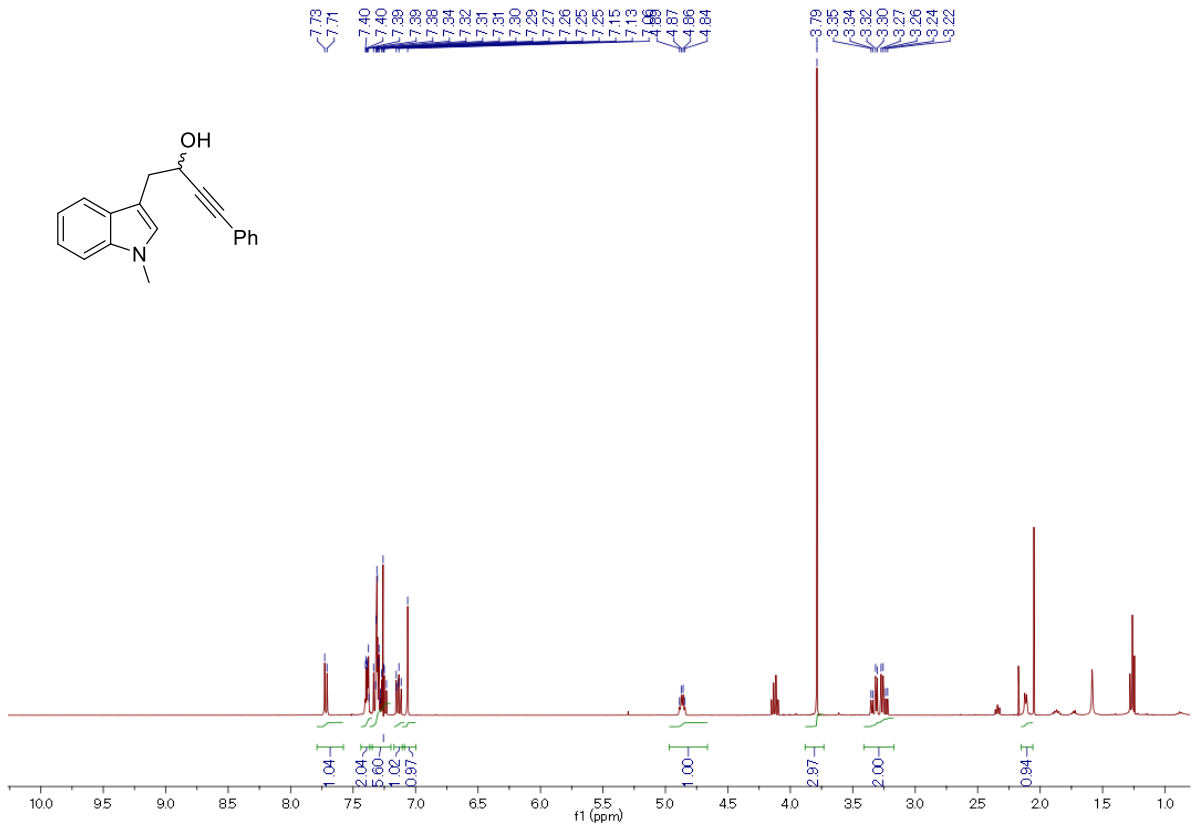
128.19
128.12
122.68
120.23
119.84
119.35
110.93
104.70
92.27
88.25
77.32
77.00
76.68
41.69
O
Ph
Ph
N
H
f1 (ppm)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Ph
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7.39
7.38
7.34
7.32
7.31
7.31
7.30
7.29
7.27
7.26
7.25
7.25
7.15
7.13
4.87
4.86
4.84
3.79
3.35
3.34
3.32
3.30
3.27
3.26
3.24
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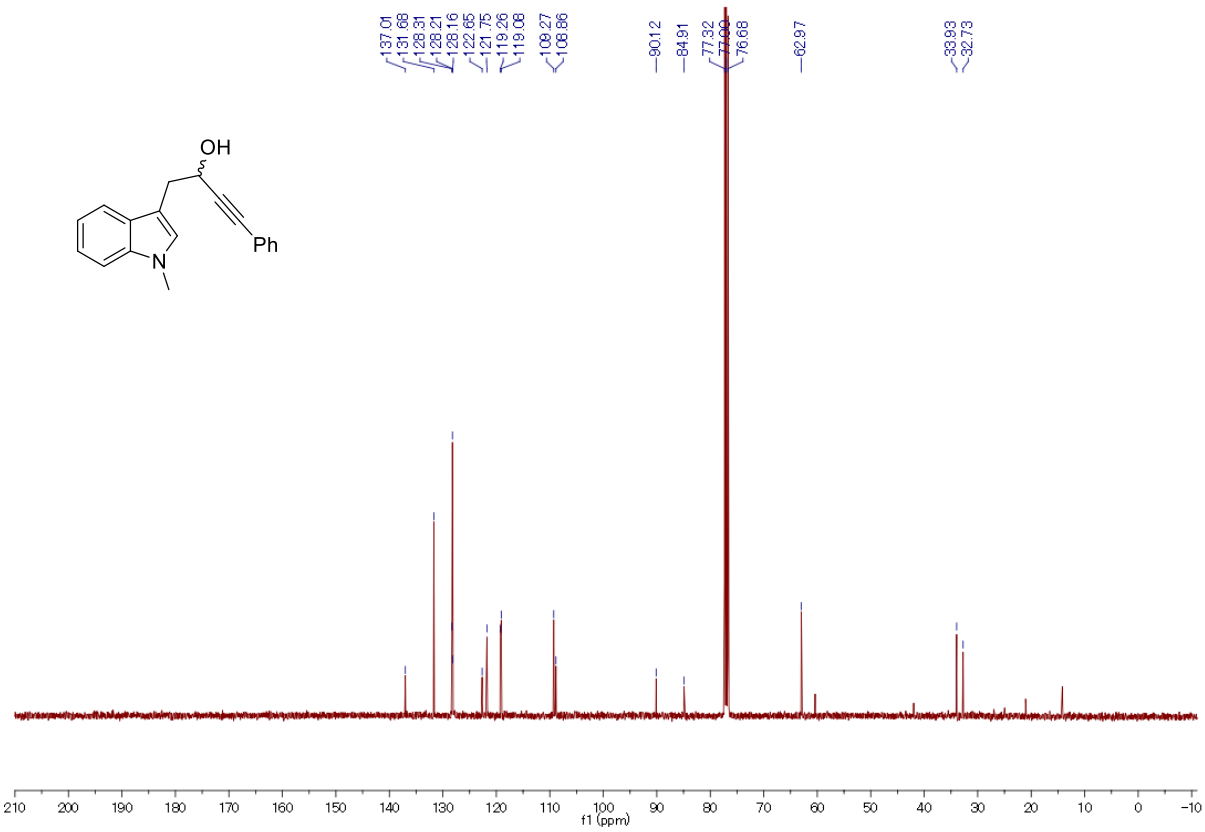
2.04
5.60
1.02
0.97
1.00
2.97
2.00
0.94
f1 (ppm)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Ph
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122.65
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119.26
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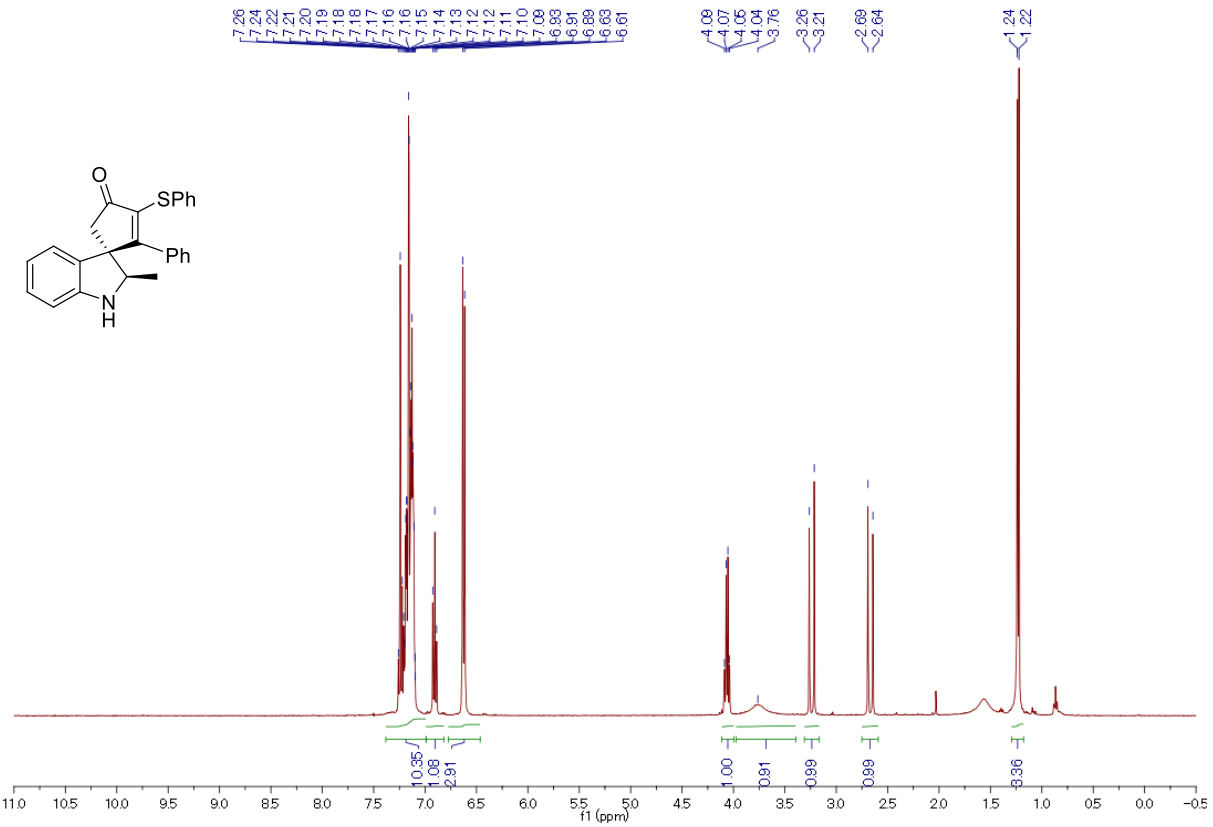
84.91
77.32
77.00
76.68
62.97
33.93
32.73
f1 (ppm)


O
SPh
Ph
N
H
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7.18
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7.16
7.16
7.15
7.14
7.13
7.12
7.12
7.11
7.10
7.08
6.83
6.91
6.89
6.63
6.61
4.09
4.07
4.05
4.04
3.76
3.26
3.21
2.69
2.64
1.24
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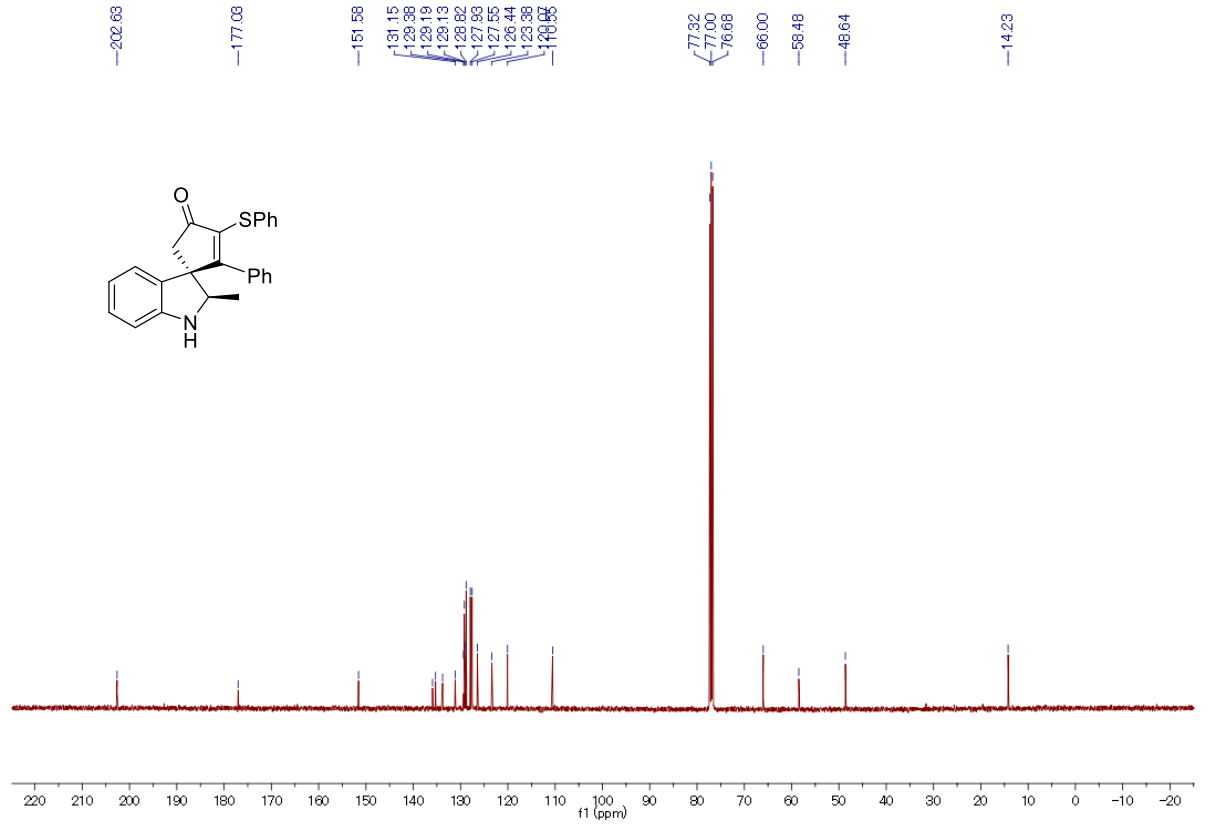
10.35
1.08
2.91
1.00
0.91
0.99
0.99
3.36
f1 (ppm)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SPh
Ph
N
H
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129.38
129.19
129.13
128.82
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127.55
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123.38
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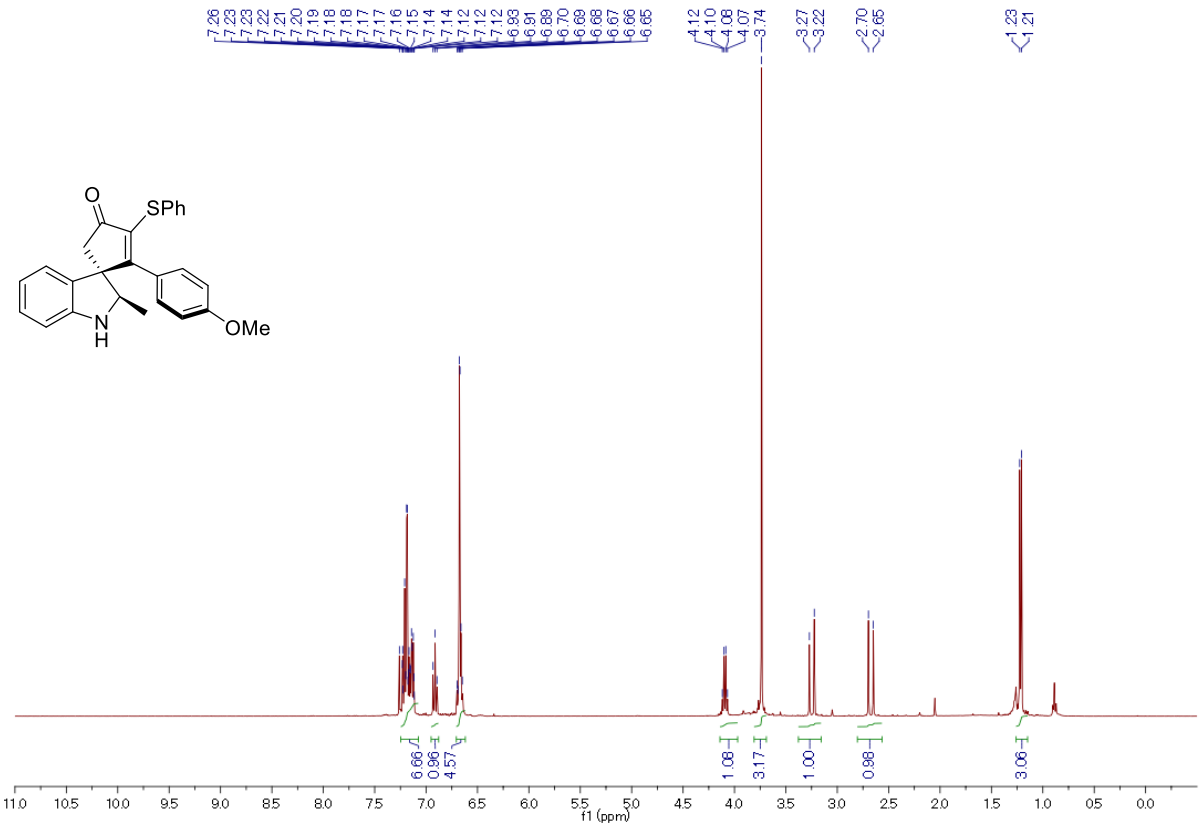
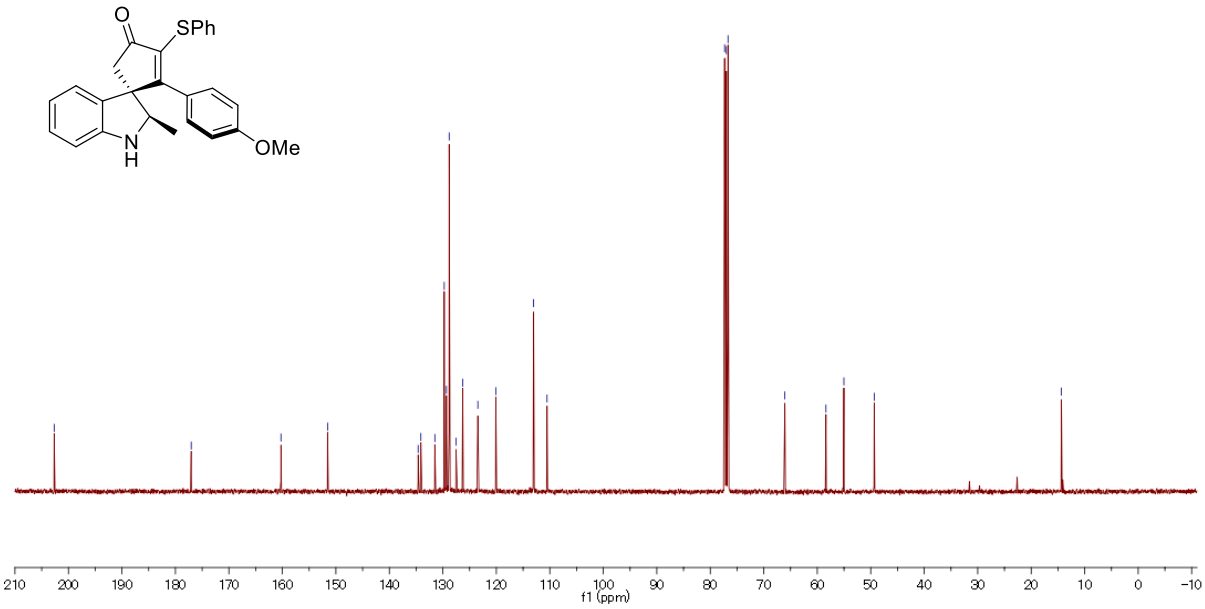
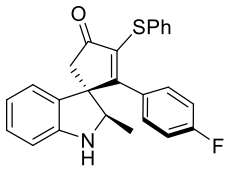
77.00
76.68
66.00
58.48
48.64
14.23
f1 (ppm)


O
SPh
N
H
OMe
f1 (ppm)


O
SPh
N
H
OMe
f1 (ppm)


O
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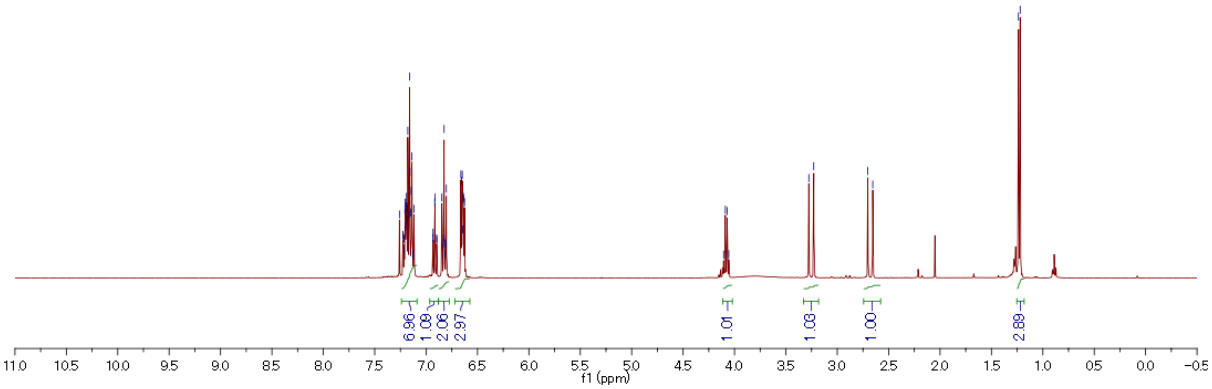
H
F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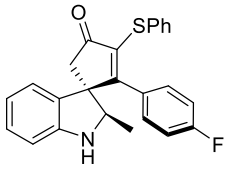
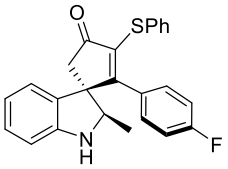
2.89
f1 (ppm)


O
SPh
N
H
F

f1 (ppm)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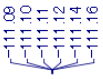
F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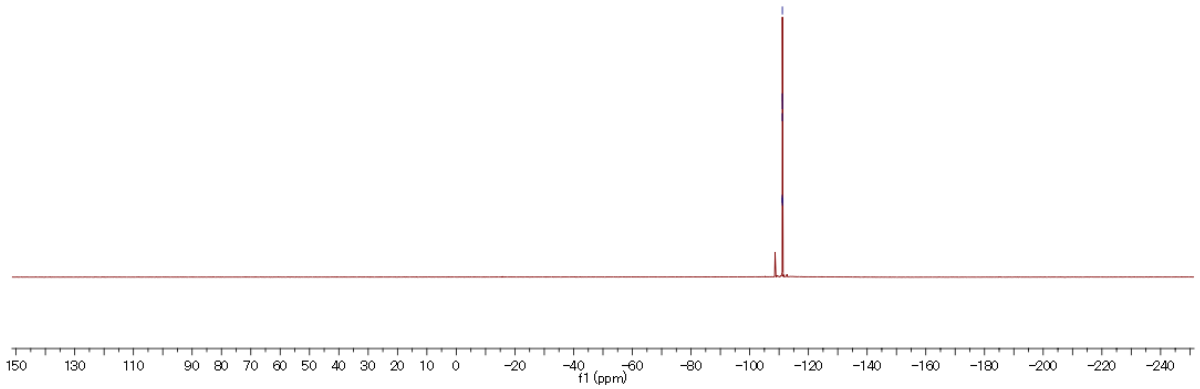
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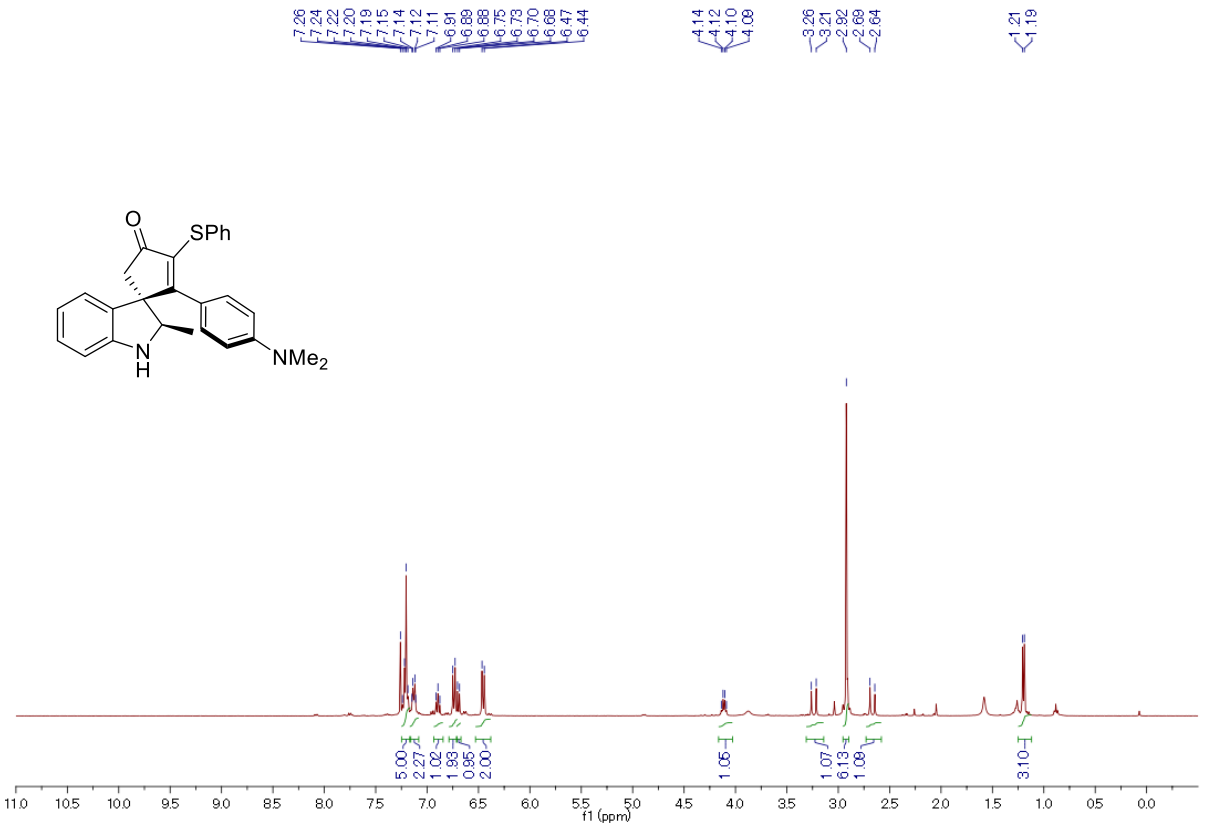
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6.75
6.73
6.70
6.68
6.47
6.44
4.14
4.12
4.10
4.09
3.26
3.21
2.92
2.69
2.64
1.21
1.19
O
SPh
N
H
NMe2
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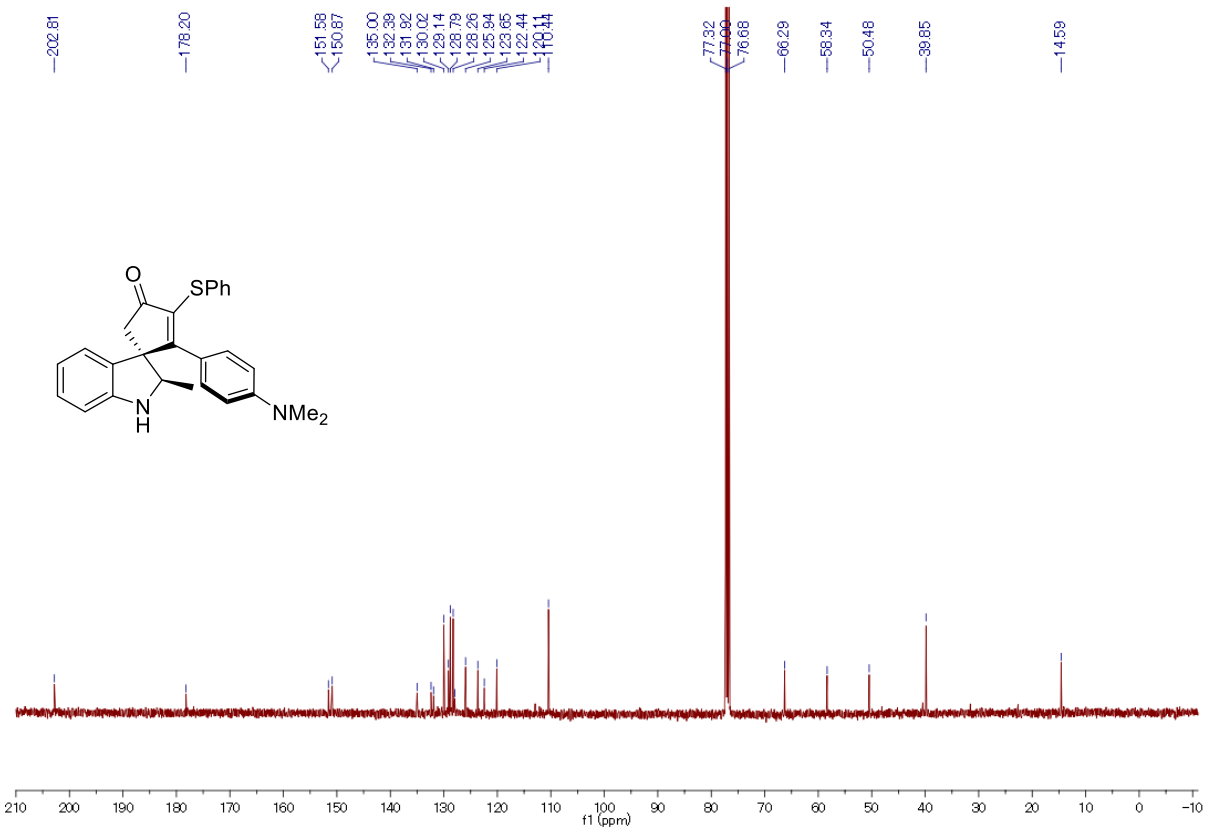
1.07
6.13
1.08
3.10
f1 (ppm)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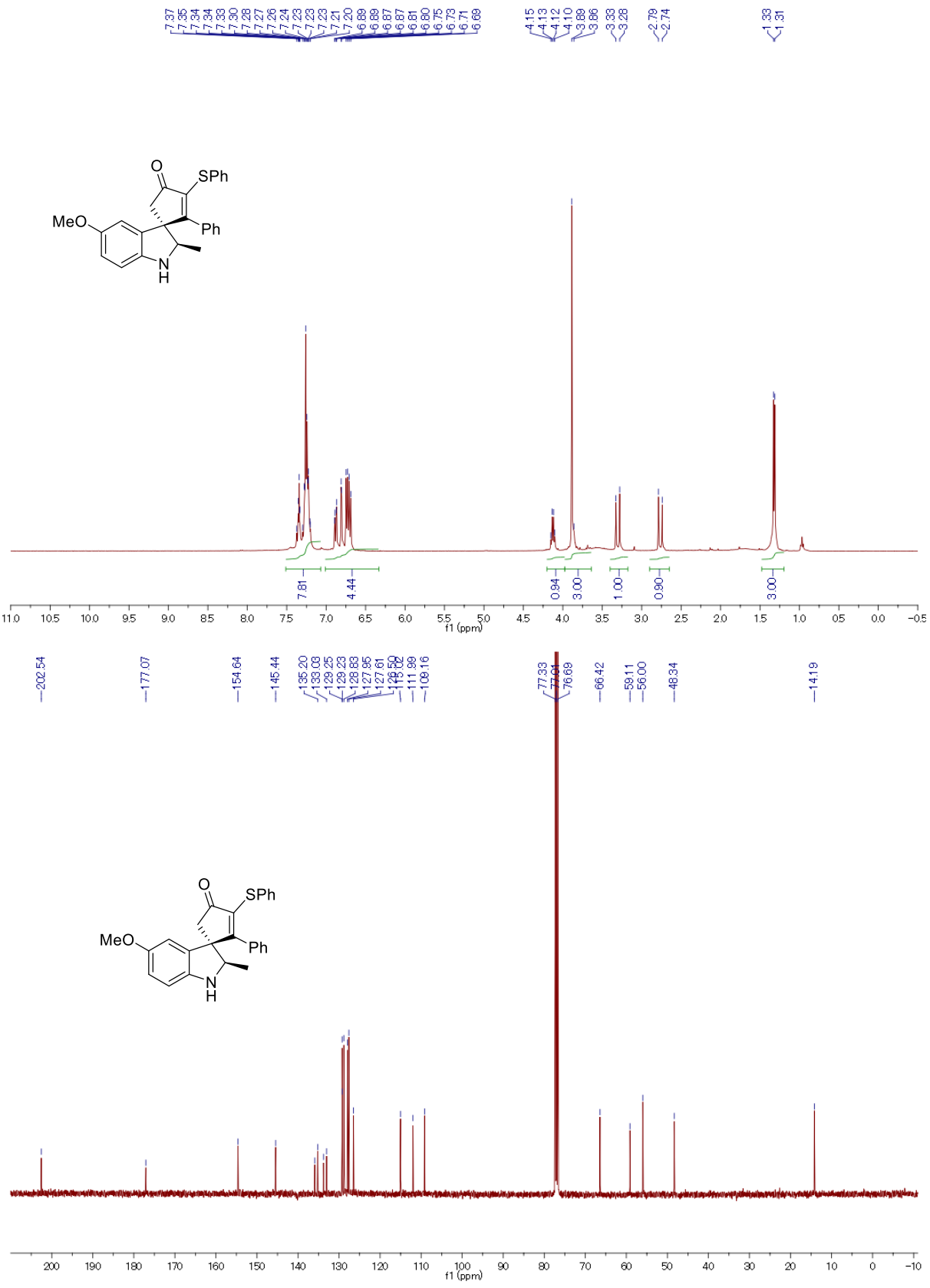
SPh
N
H
NMe2
f1 (ppm)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6.81
6.80
6.75
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6.71
6.69
4.15
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4.12
4.10
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3.28
2.79
2.74
1.33
1.31
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SPh
MeO
Ph
N
H
7.81
4.44
0.84
3.00
1.00
0.90
3.00
f1 (ppm)
202.54
177.07
154.64
145.44
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133.09
129.25
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128.83
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109.16
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SPh
MeO
Ph
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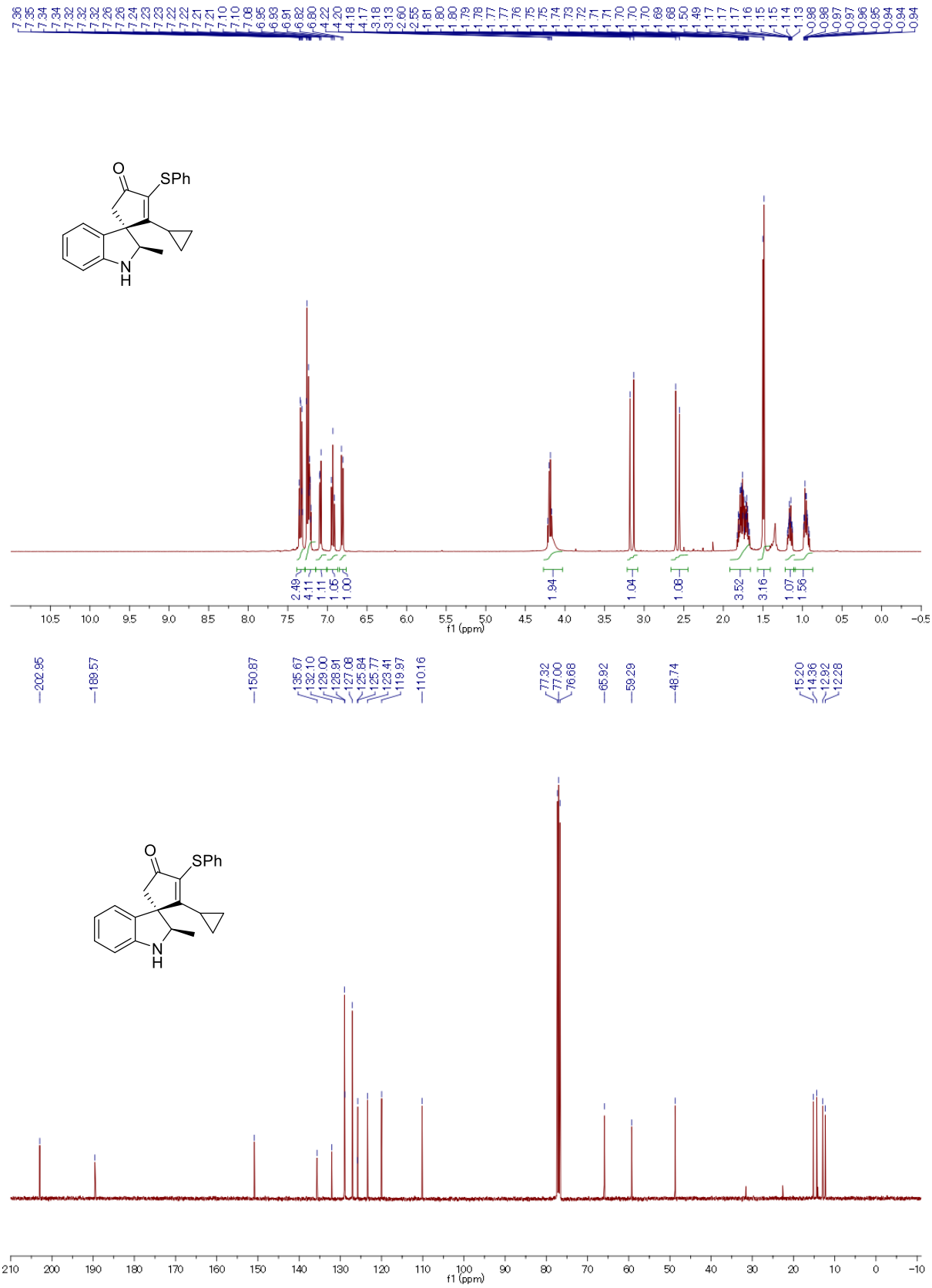
H
f1 (ppm)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7.10
7.10
7.08
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6.93
6.91
6.82
6.80
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4.18
4.17
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SPh
N
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77.00
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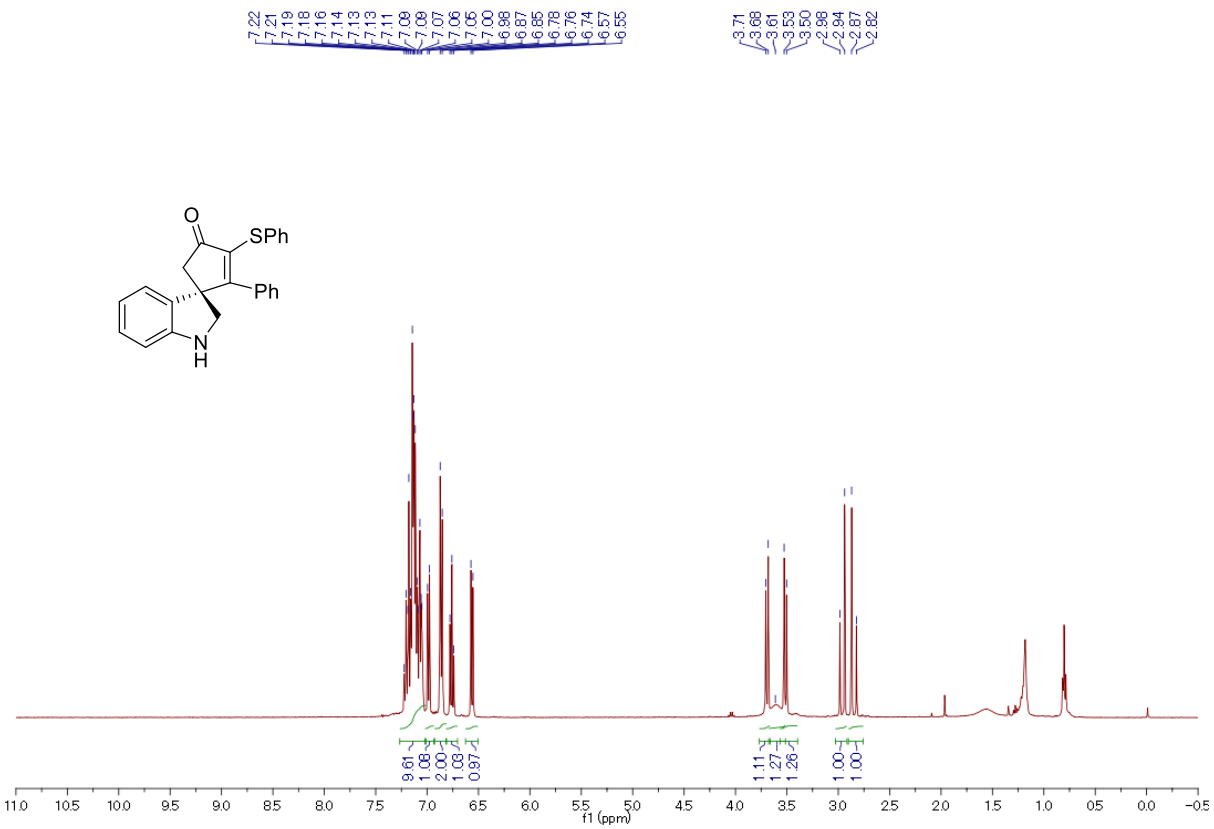
12.28
O
SPh
N
H
f1 (ppm)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3.53
3.50
2.98
2.94
2.87
2.82
O
SPh
Ph
N
H
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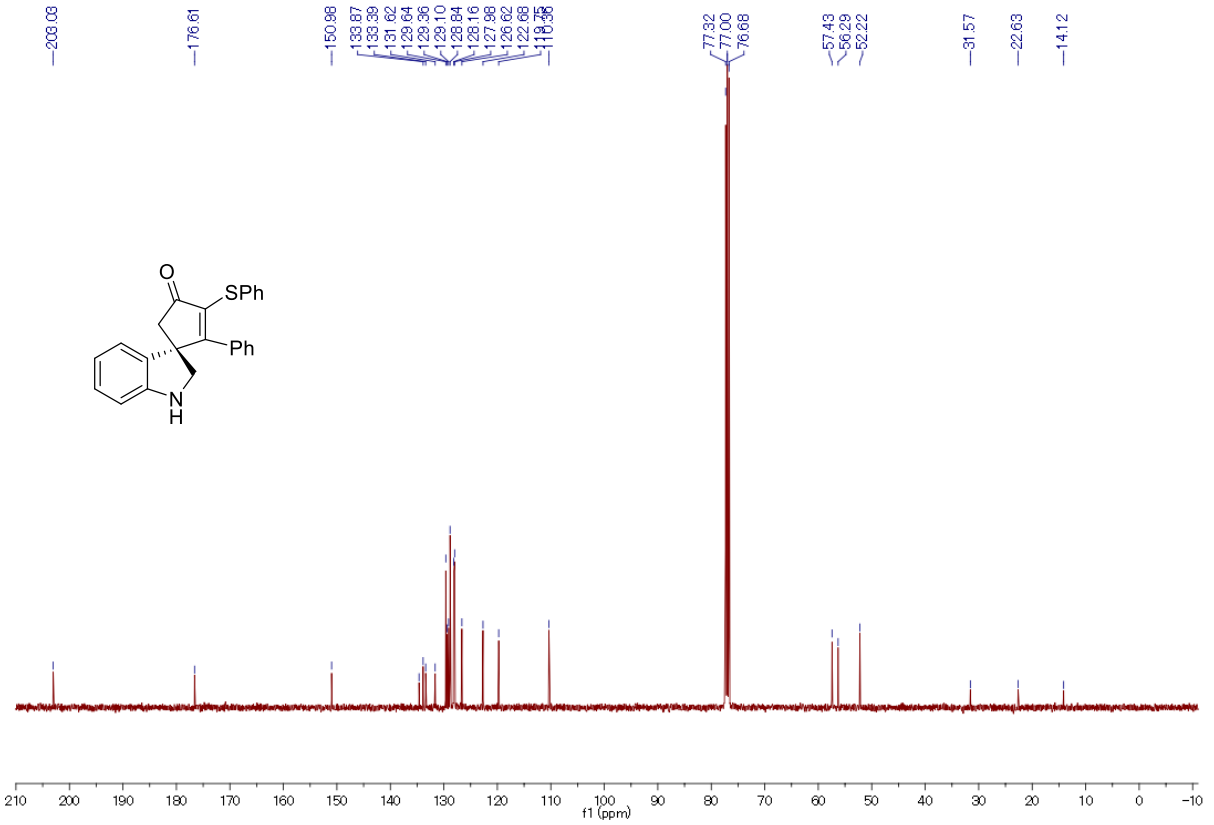
2.00
1.03
0.97
1.11
1.27
1.26
1.00
1.00
f1 (ppm)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122.68
77.32
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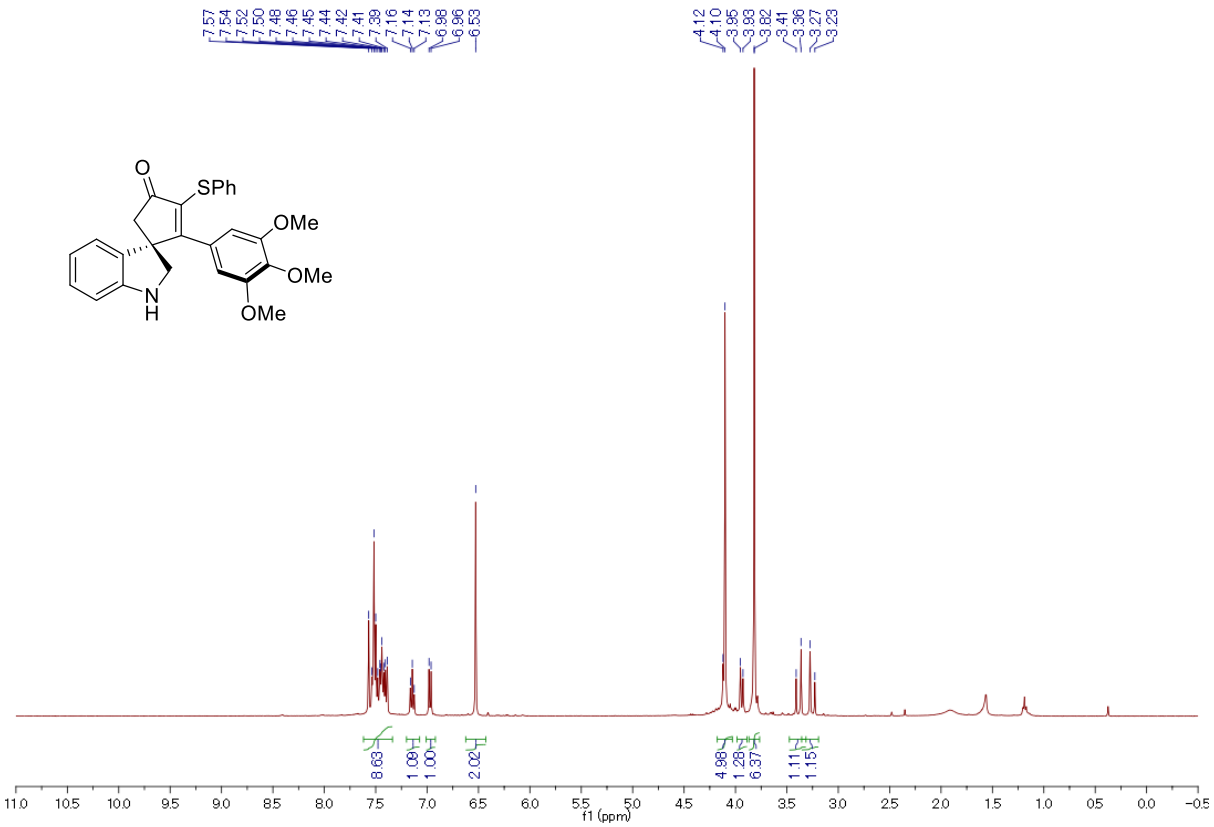
56.29
52.22
31.57
22.63
14.12
O
SPh
Ph
N
H
f1 (ppm)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7.14
7.13
6.98
6.96
6.53
4.12
4.10
3.95
3.93
3.82
3.41
3.36
3.27
3.23
O
SPh
OMe
OMe
OMe
N
H
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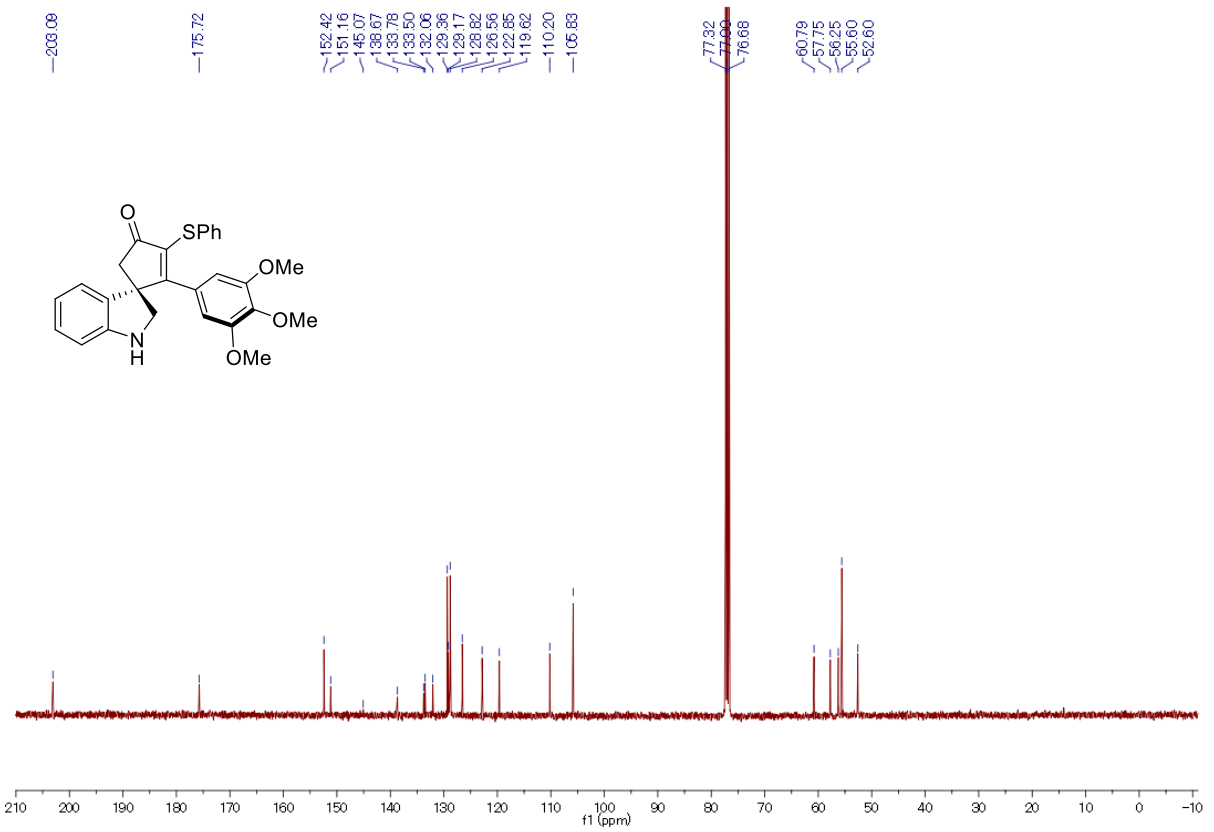
1.00
2.02
4.98
1.28
6.37
1.11
1.15
f1 (ppm)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129.36
129.17
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OMe
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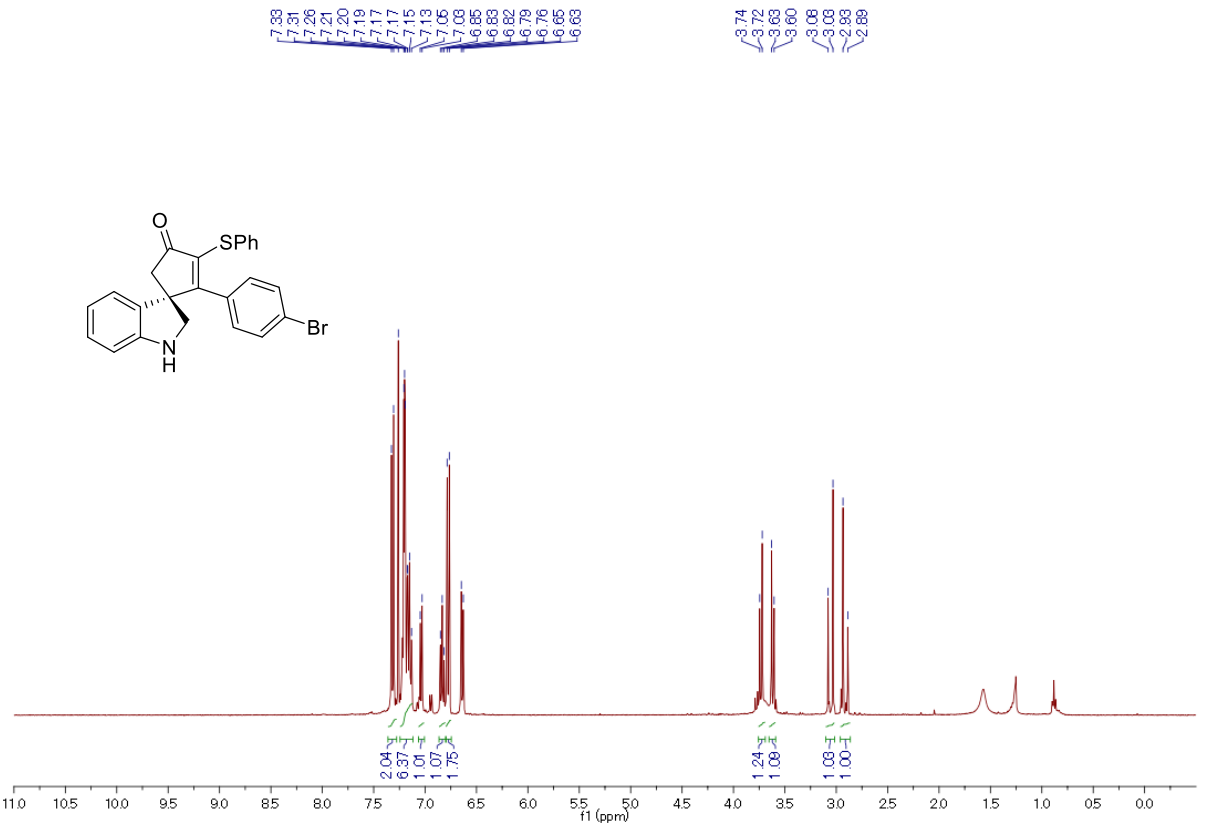
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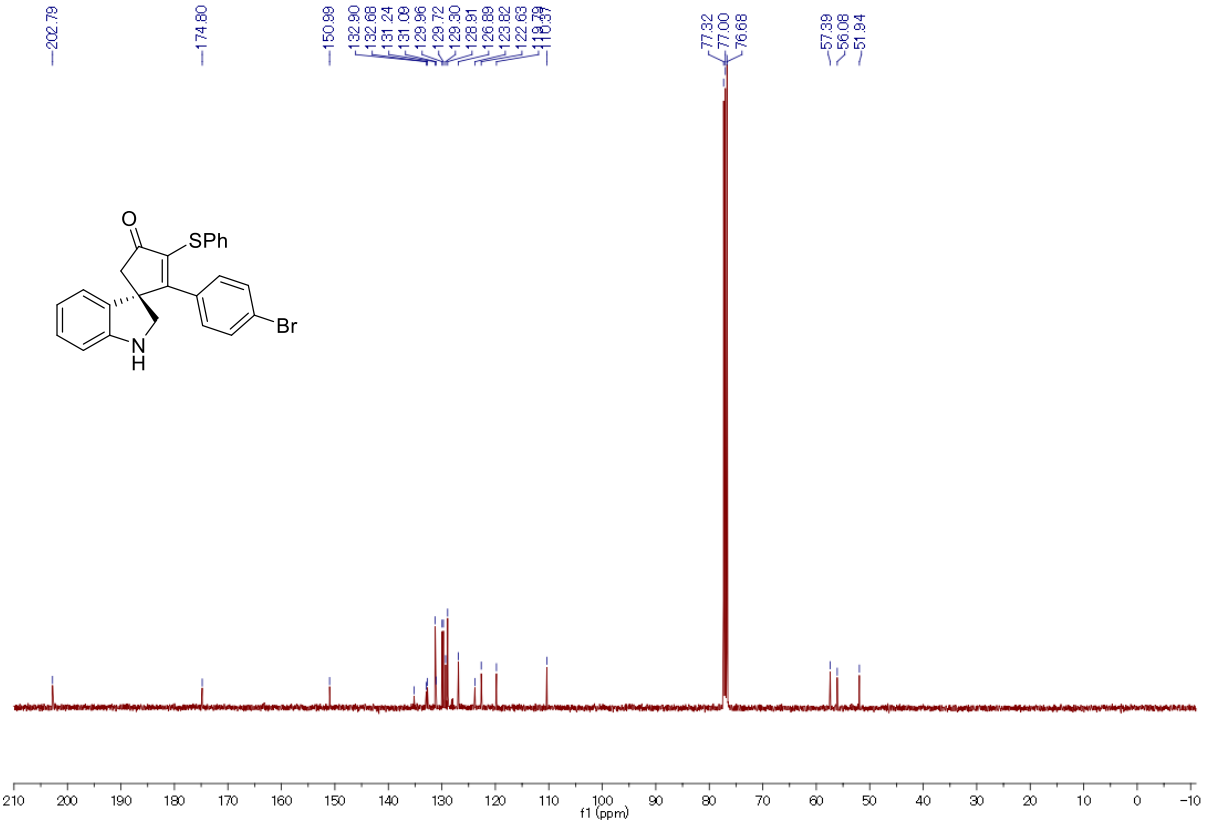
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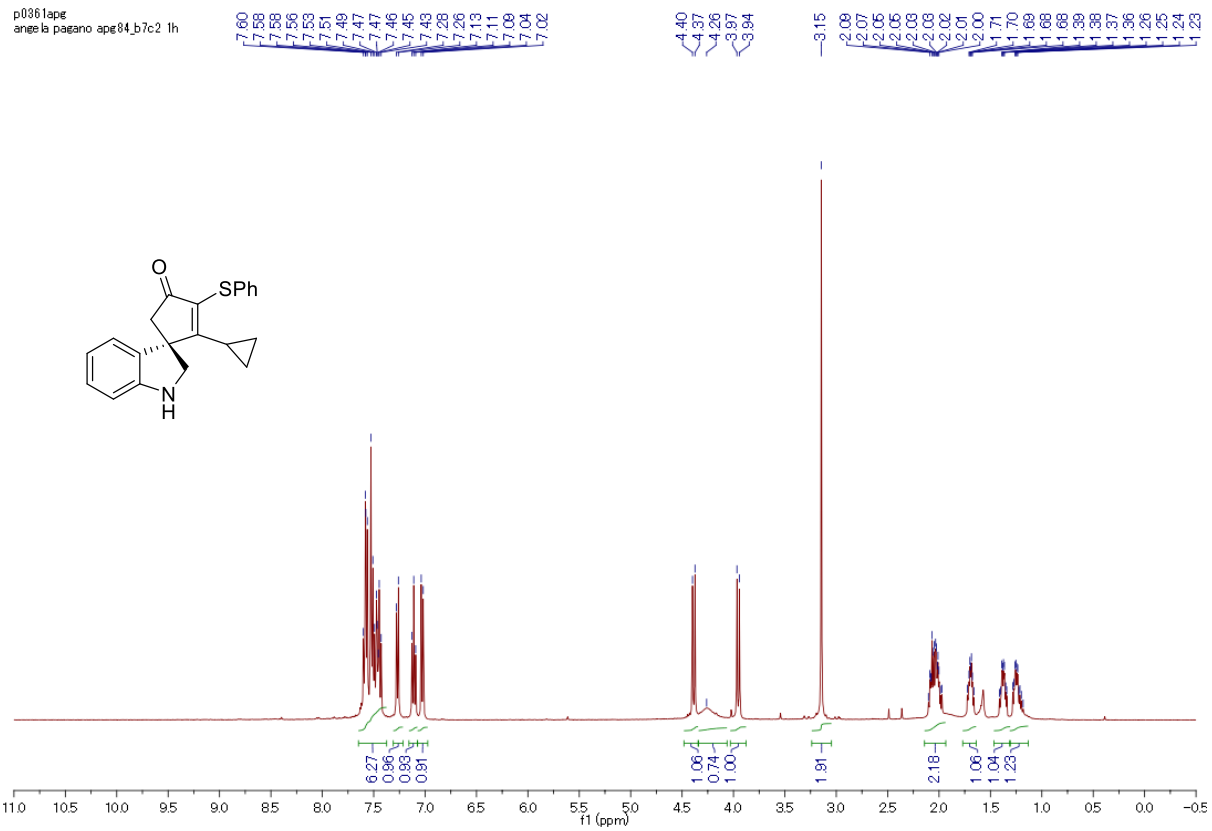
SPh
Br
N
H
f1 (ppm)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angela pagano apg84_b7c2 1h
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SPh
N
H
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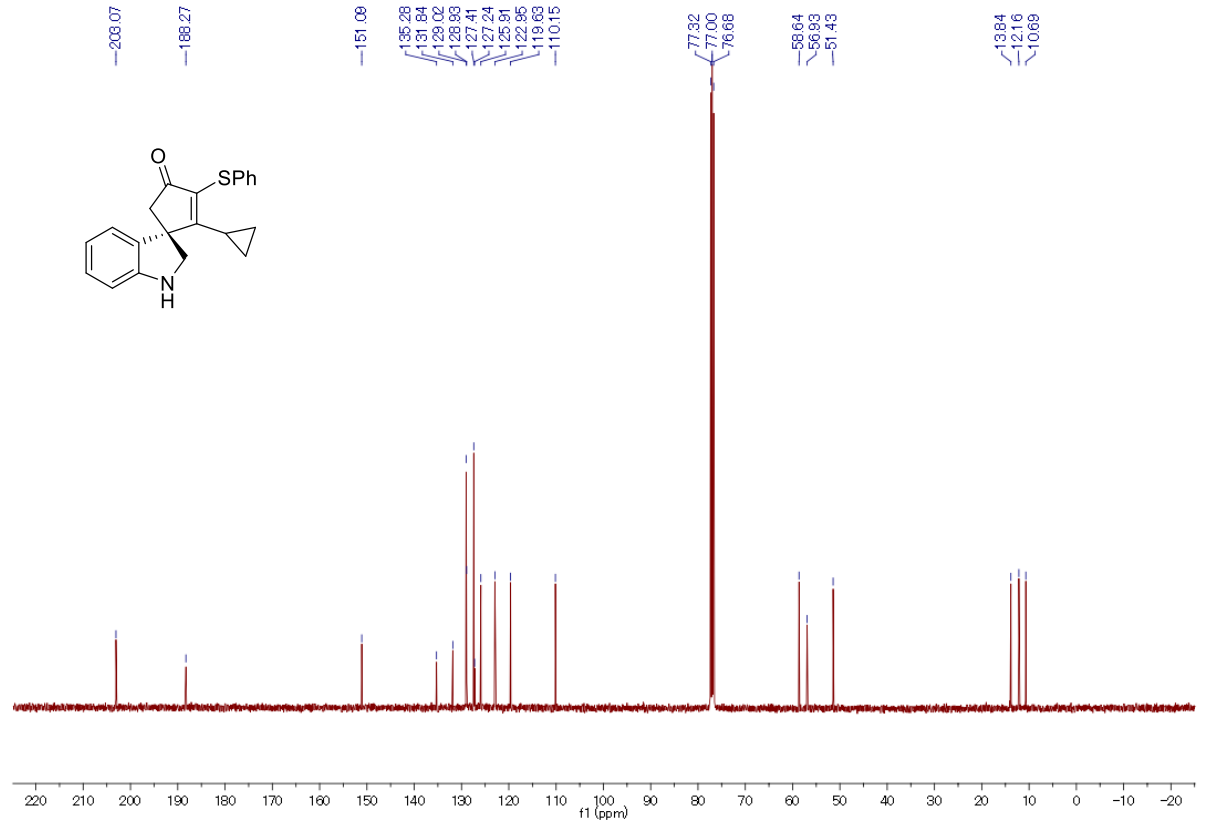
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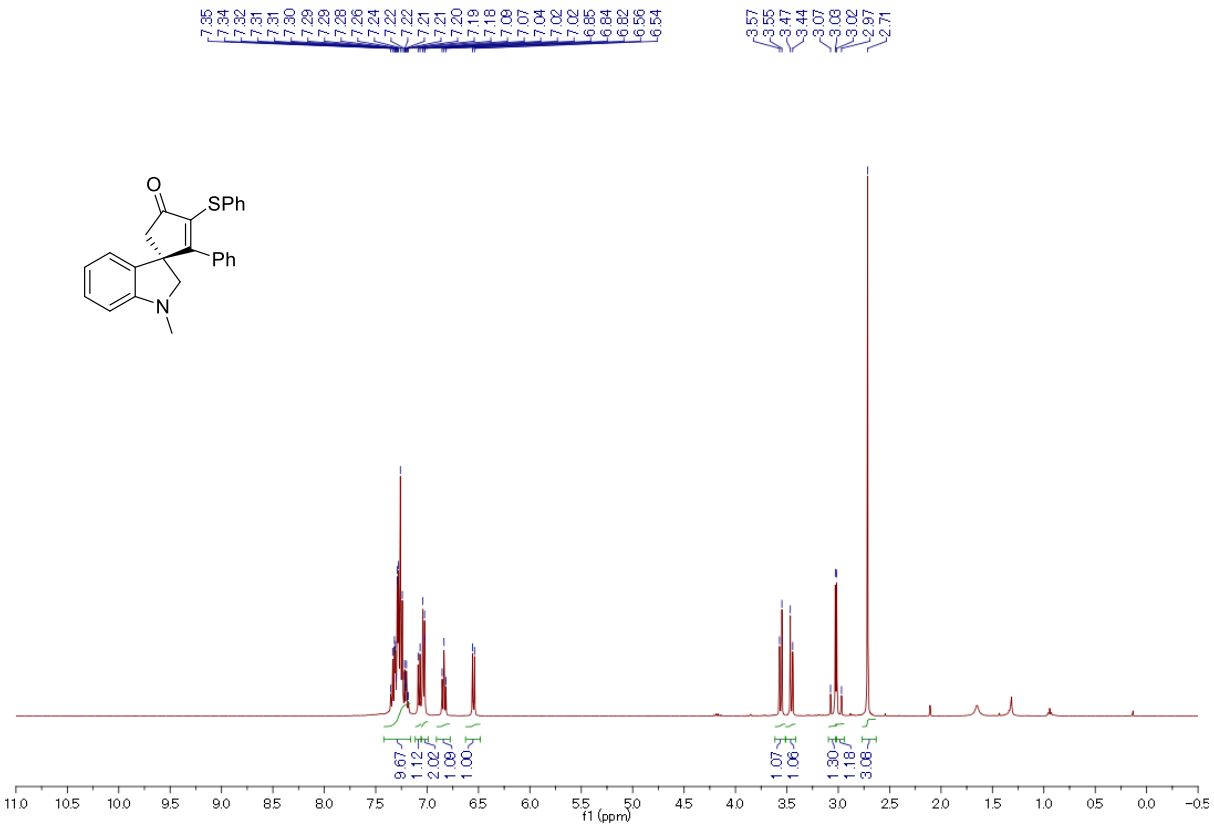
N
H
f1 (ppm)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6.56
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3.44
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3.03
3.02
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2.71
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SPh
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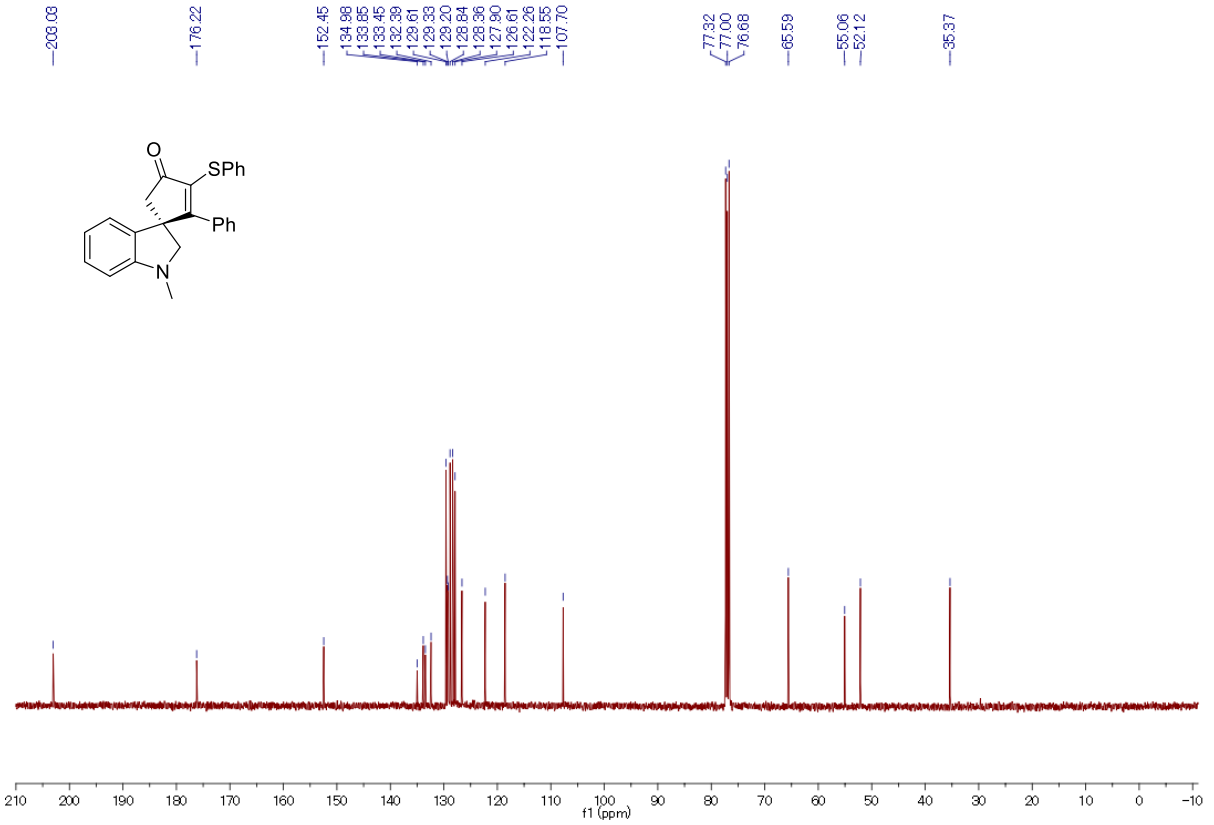
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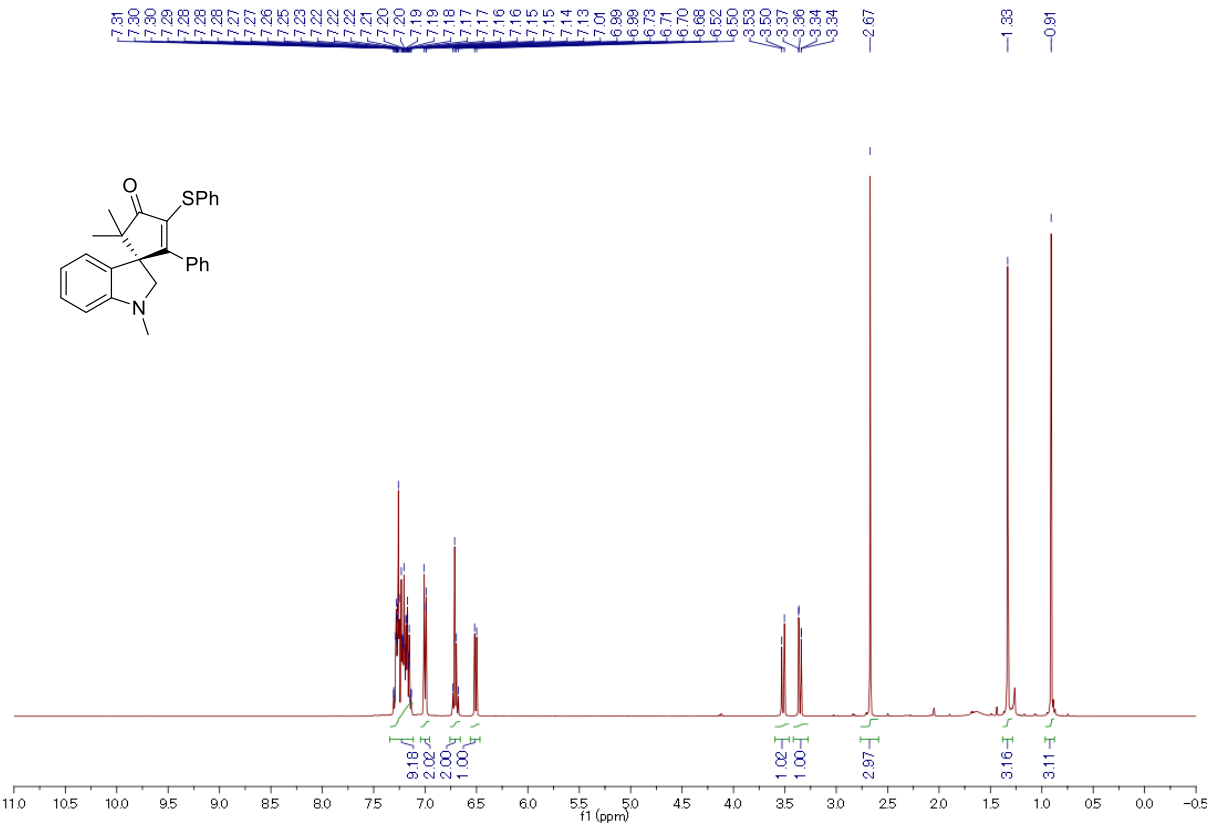
N
f1 (ppm)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7.15
7.15
7.14
7.13
7.01
6.99
6.99
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6.71
6.70
6.68
6.52
6.50
3.53
3.50
3.37
3.36
3.34
3.34
2.67
1.33
0.91
O
SPh
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3.11
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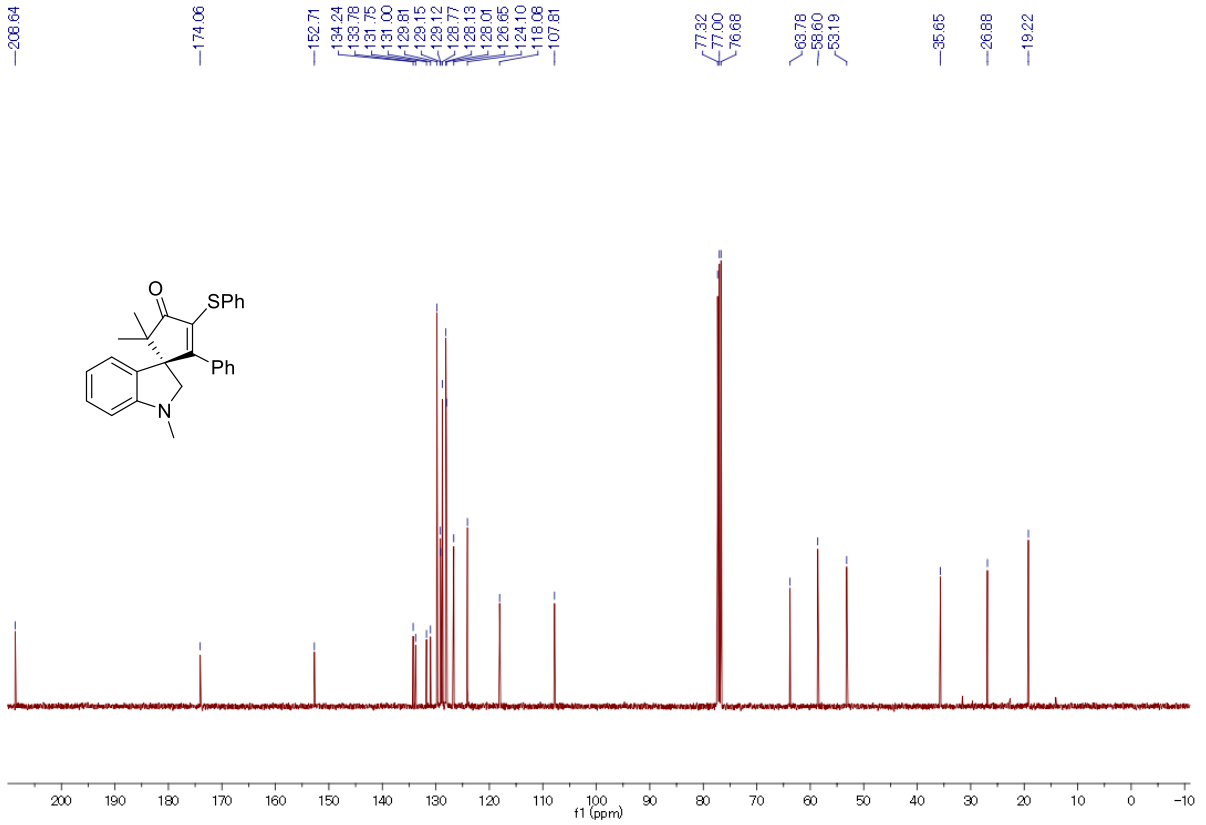
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19.22
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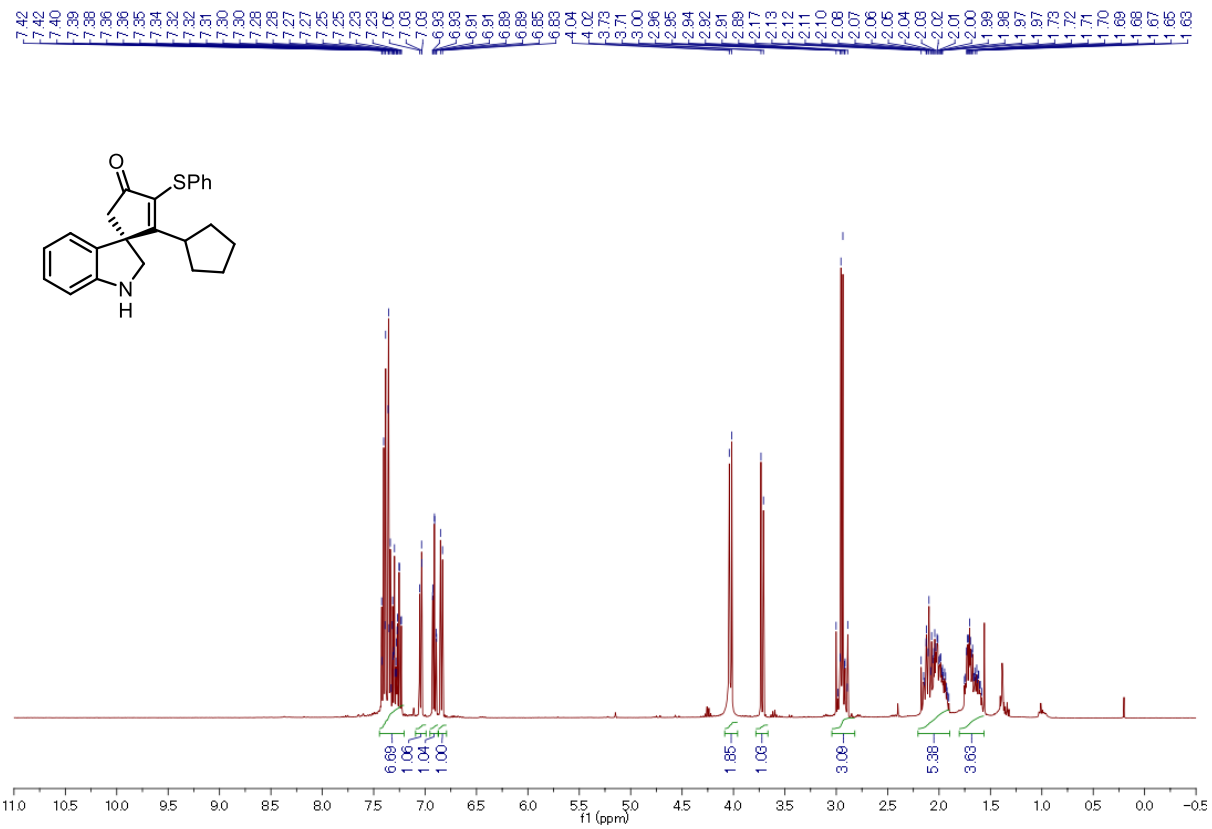
SPh
Ph
N
f1 (ppm)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O
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N
H
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1.00
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1.03
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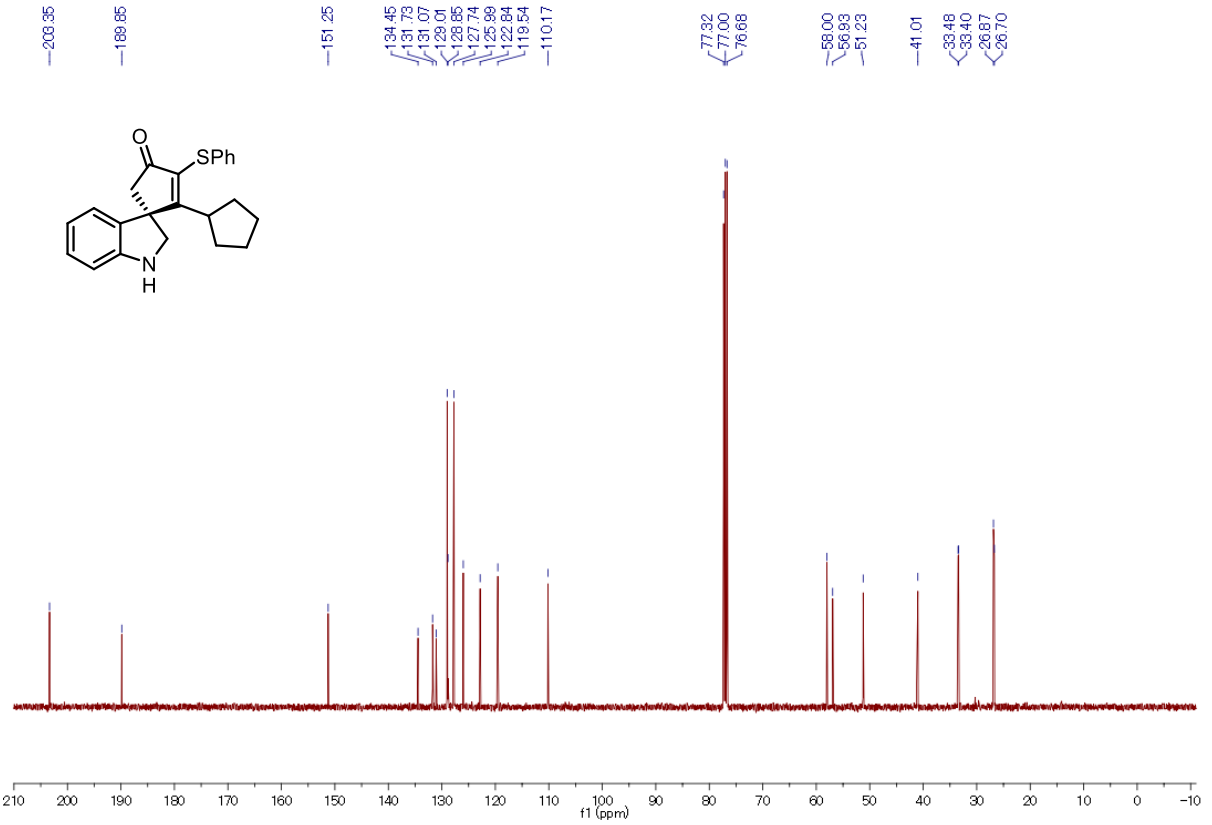
3.63
f1 (ppm)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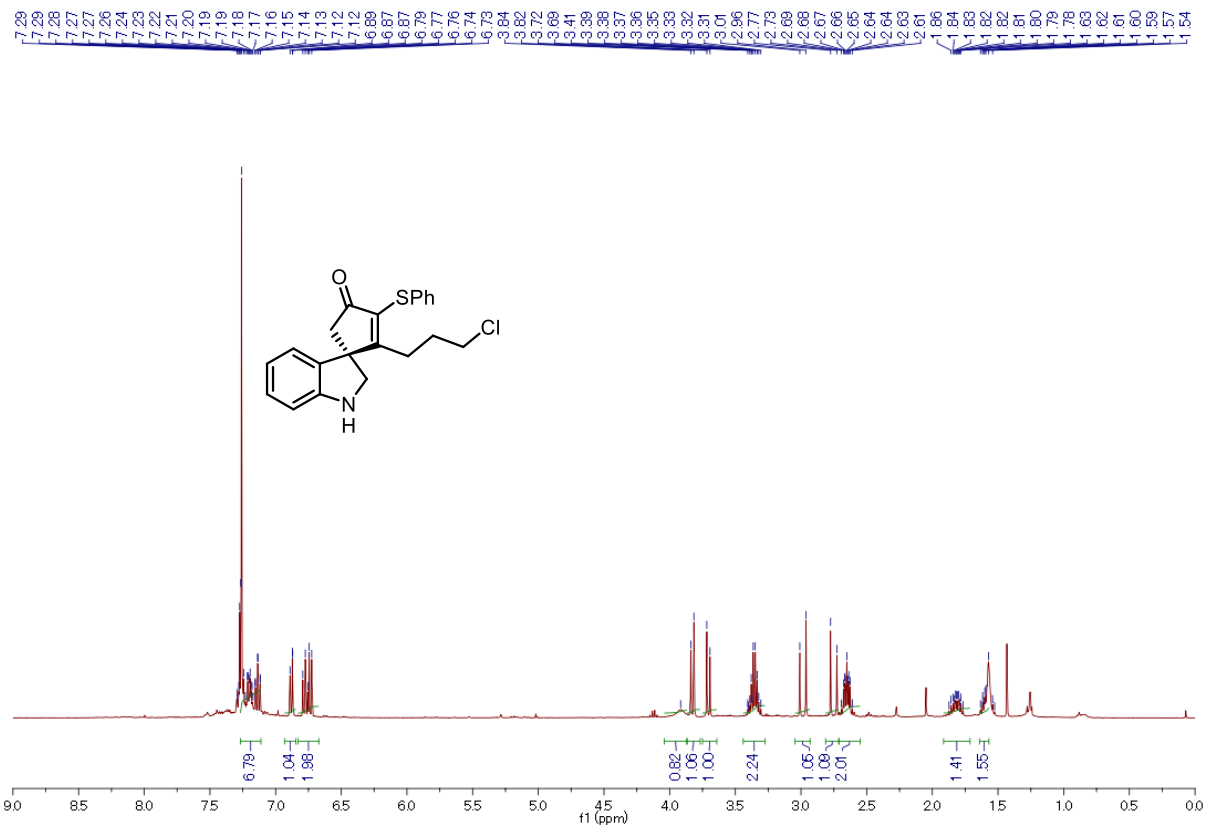
O
SPh
N
H
f1 (ppm)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1.62
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1.60
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1.54
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SPh
Cl
N
H
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2.01
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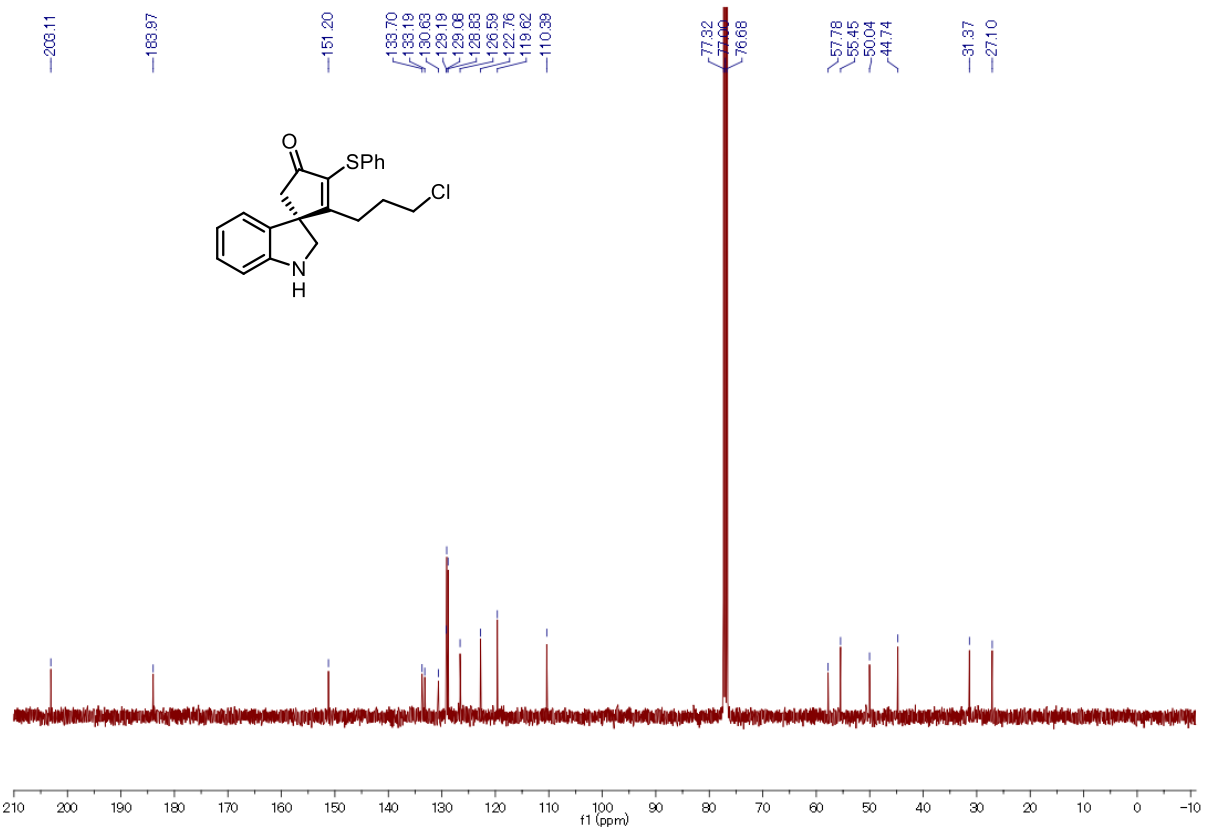
1.55
f1 (ppm)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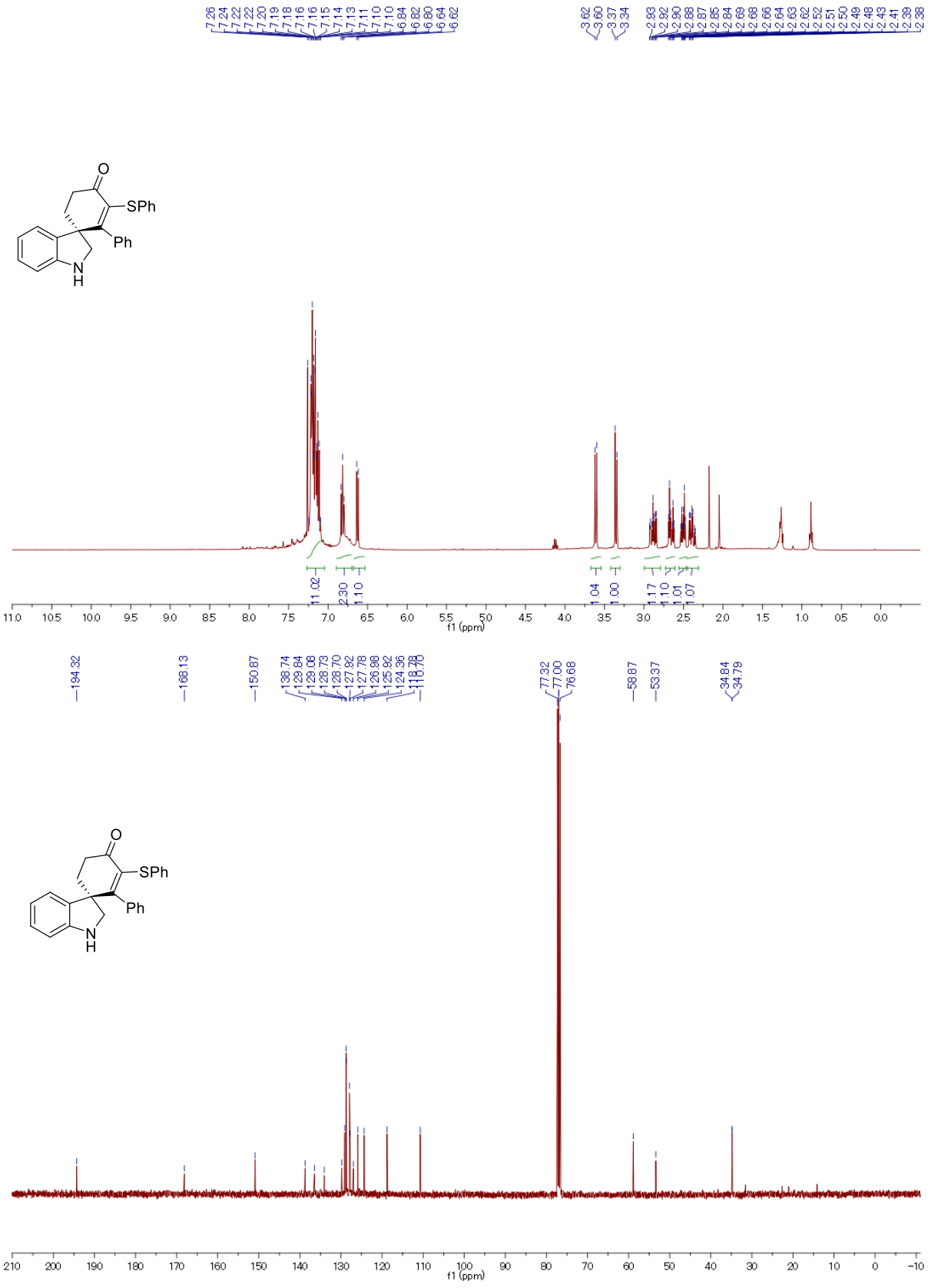
f1 (ppm)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SPh
Ph
N
H
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1.00
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1.10
1.01
1.07
f1 (ppm)
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129.06
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126.98
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O
SPh
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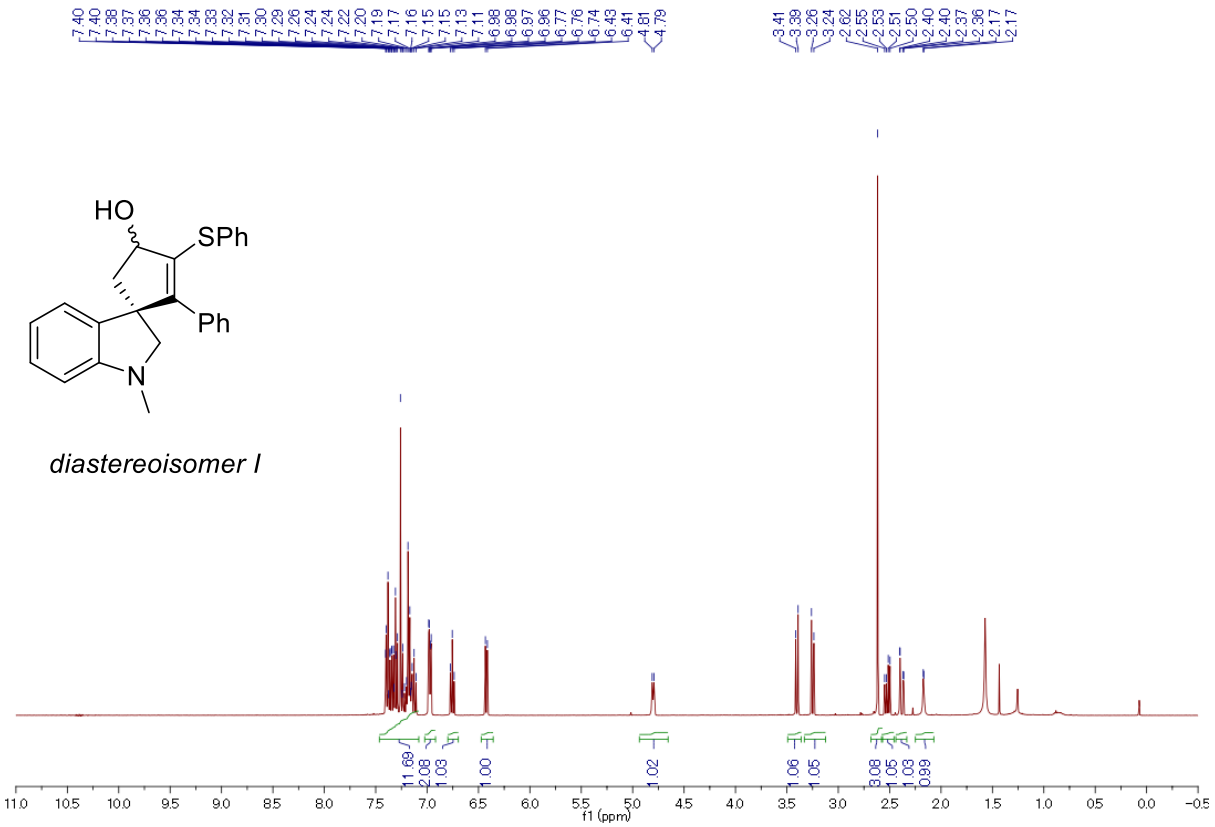
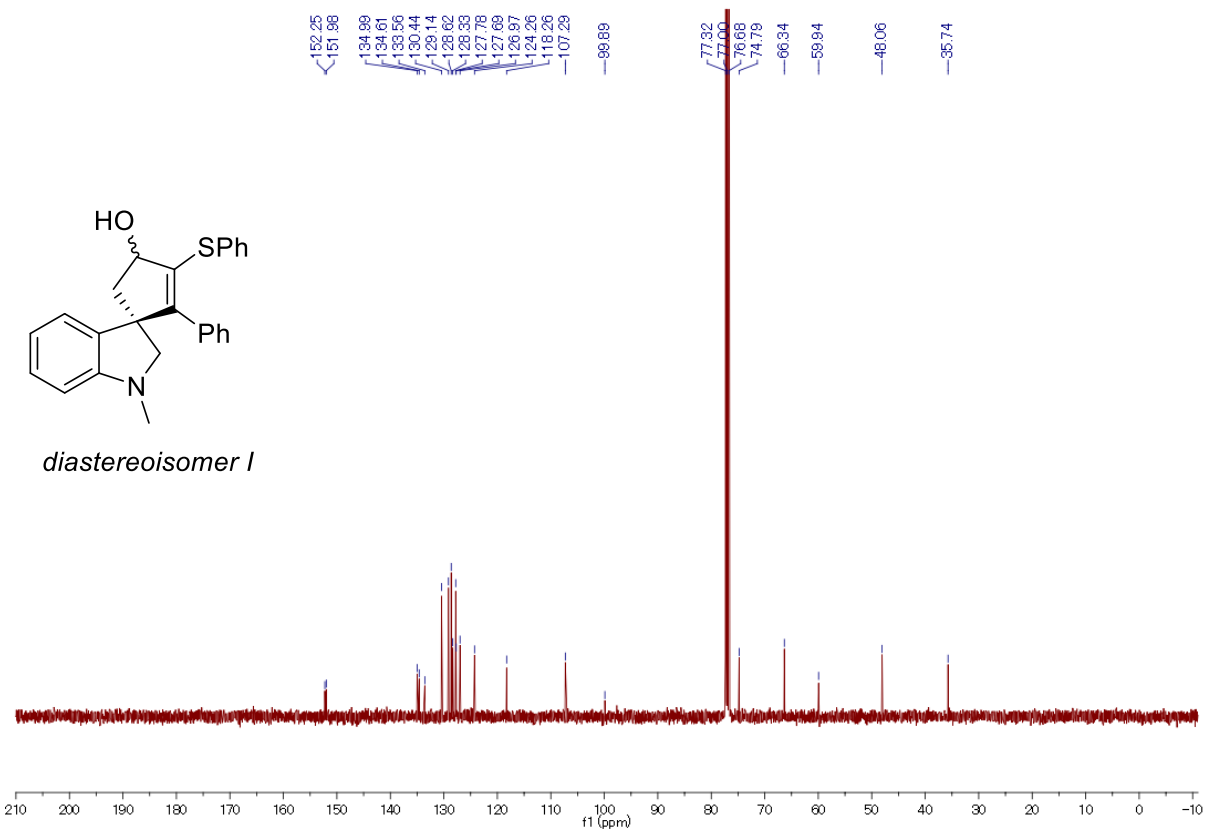
N
H
f1 (ppm)


HO
SPh
Ph
N
diastereoisomer I


HO
SPh
Ph
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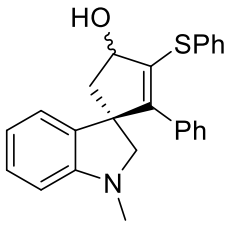
diastereoisomer I



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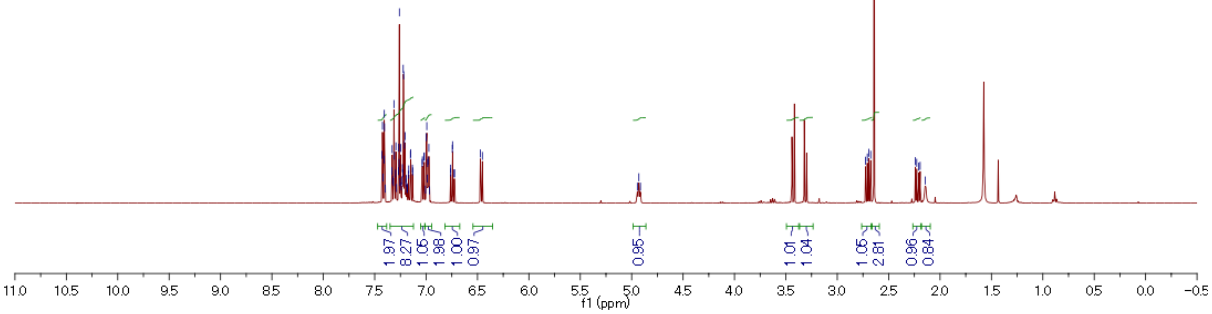
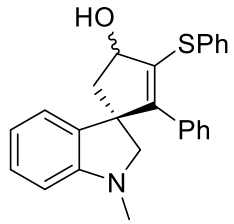
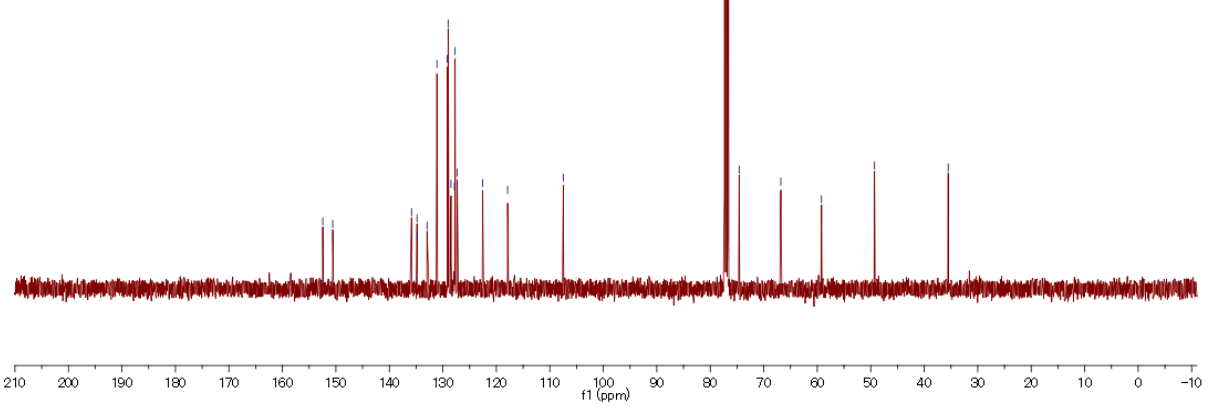
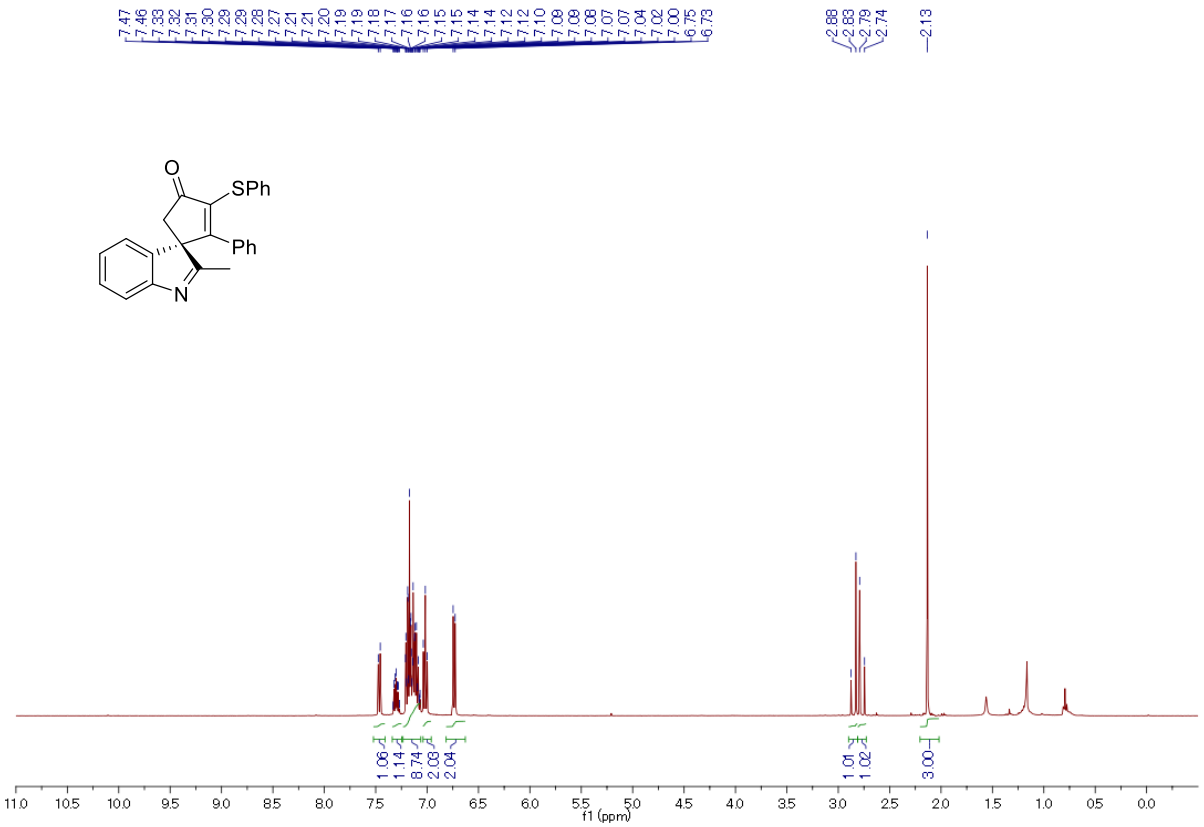




diastereoisomer II

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7.08
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7.02
7.00
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2.79
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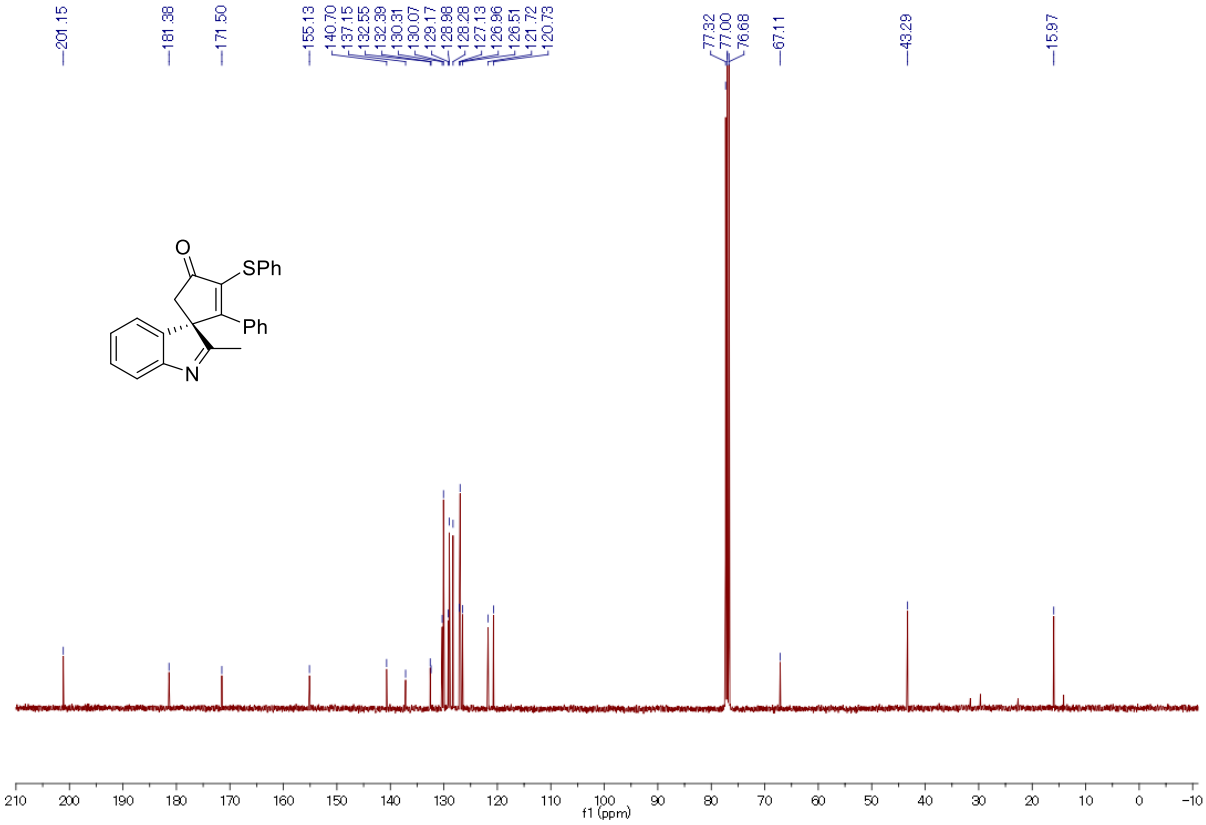
f1 (ppm)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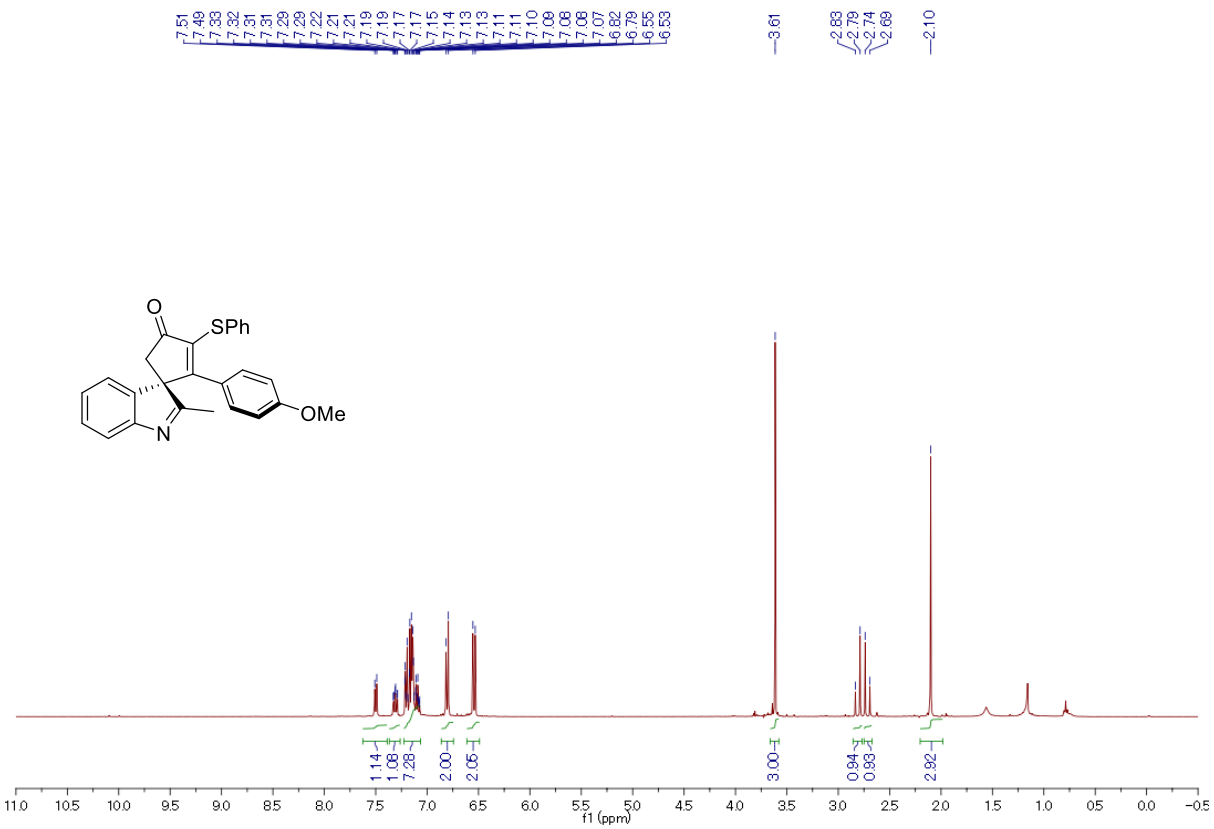
SPh
Ph
N
f1 (ppm)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O
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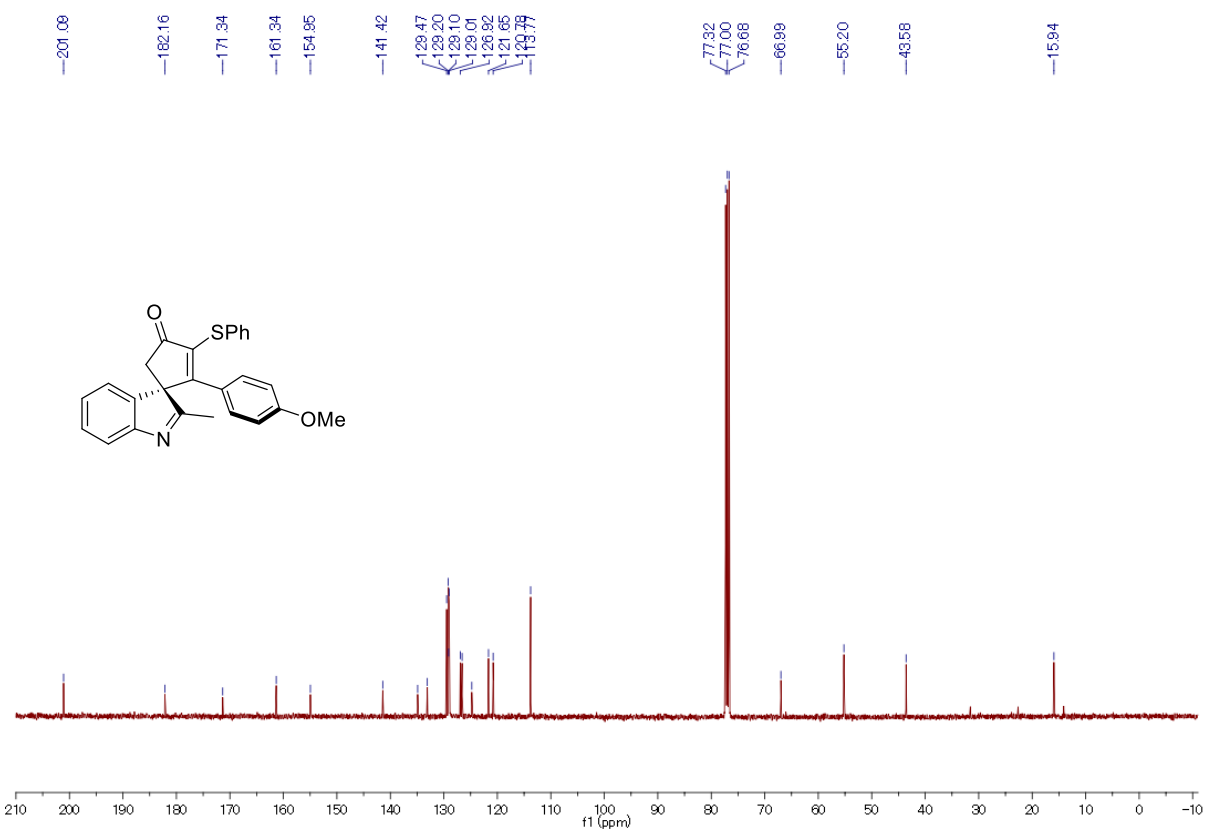
f1 (ppm)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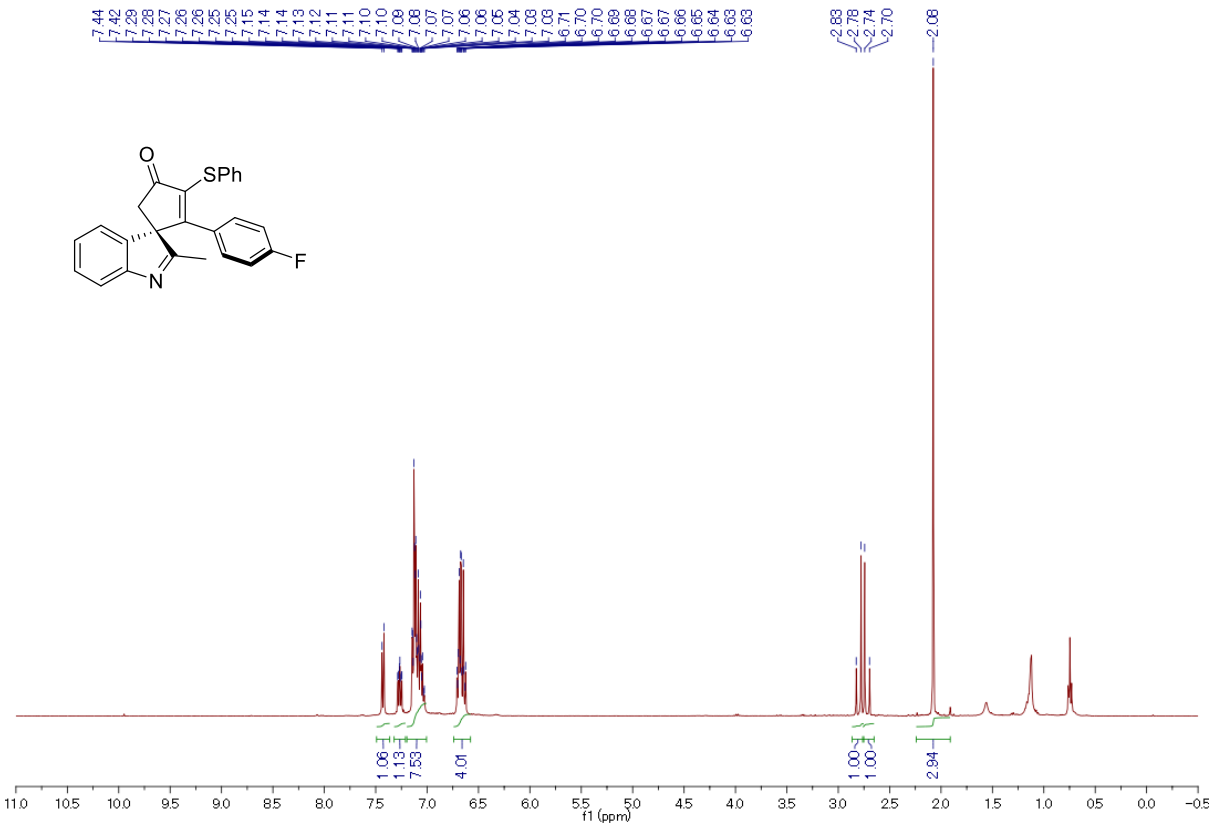
43.58
15.94
O
SPh
OMe
N
f1 (ppm)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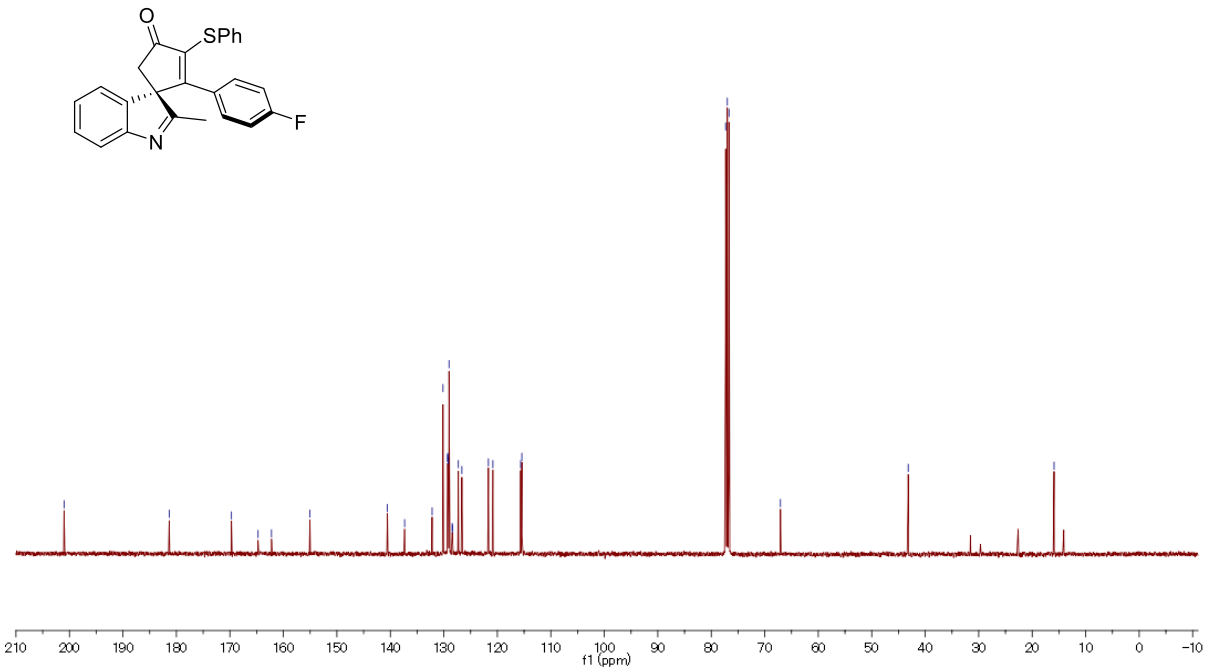
SPh
F
N
f1 (ppm)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SPh
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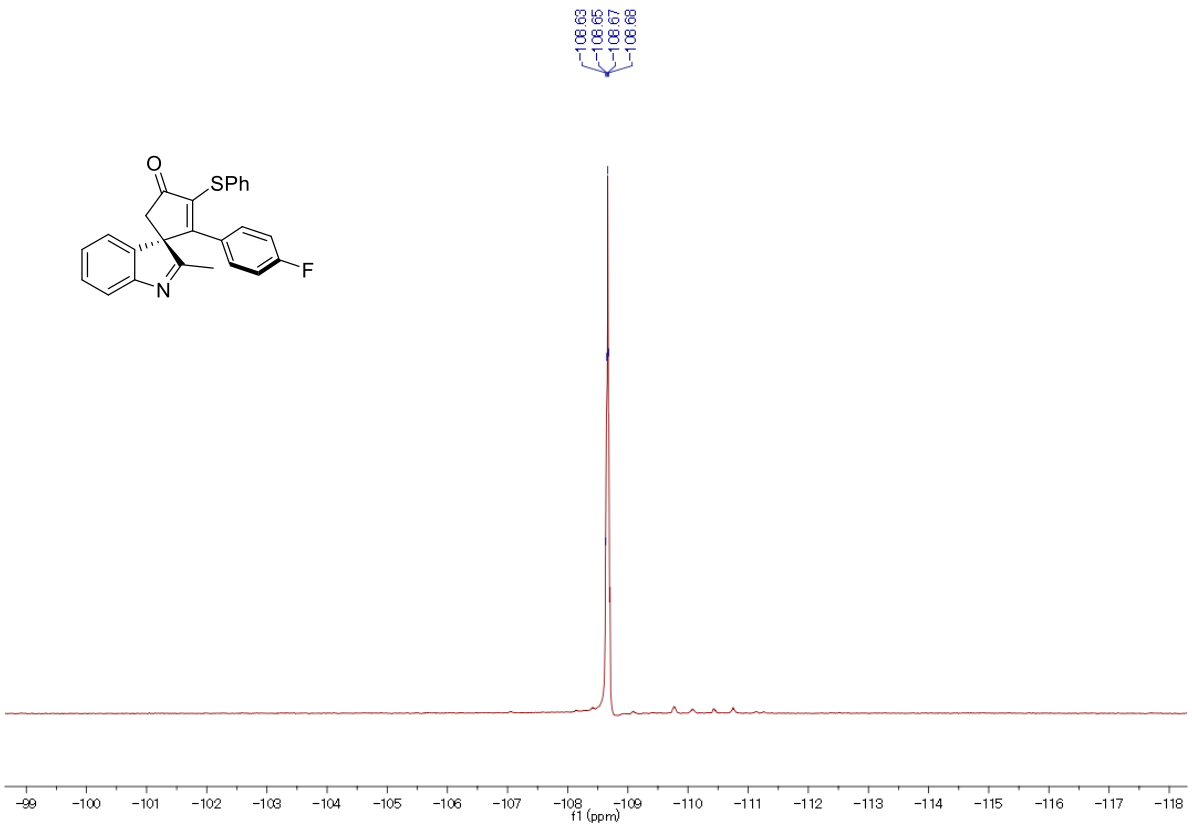
N
f1 (ppm)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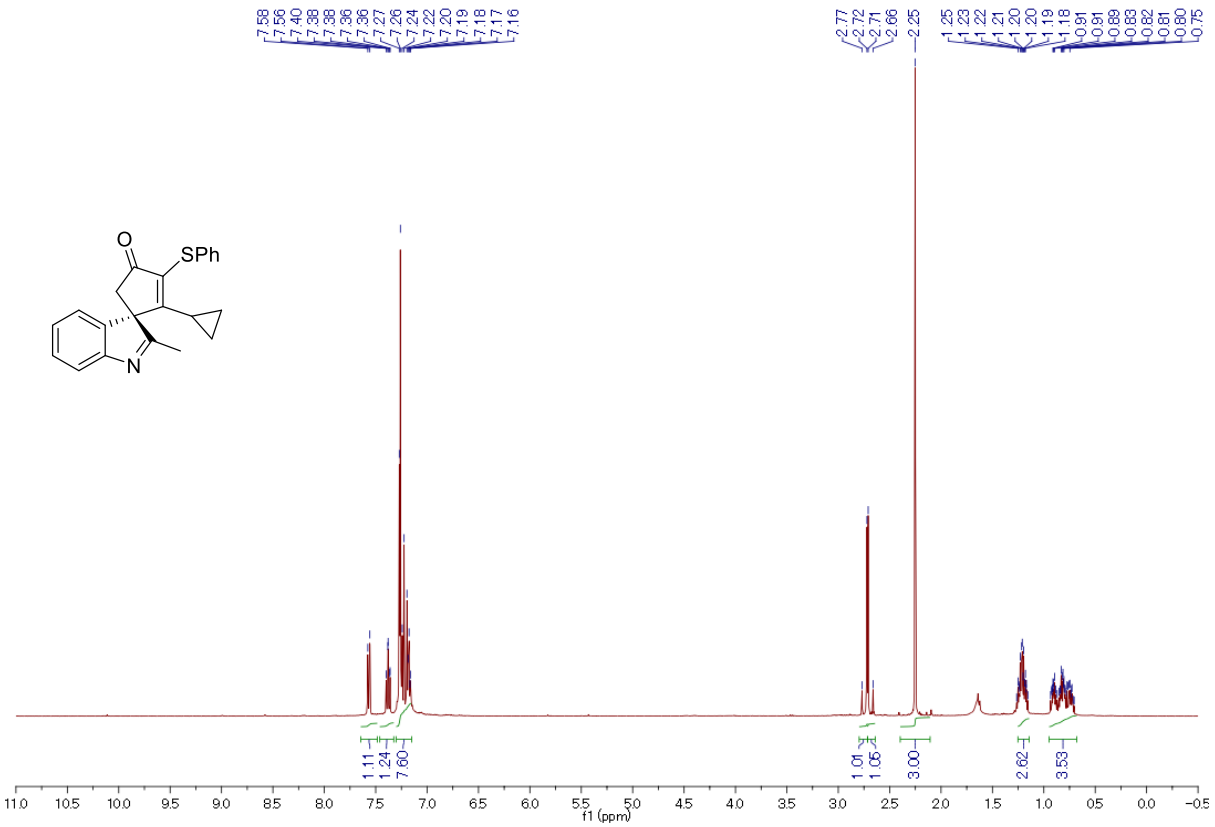
f1 (ppm)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1.23
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1.19
1.18
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0.91
0.89
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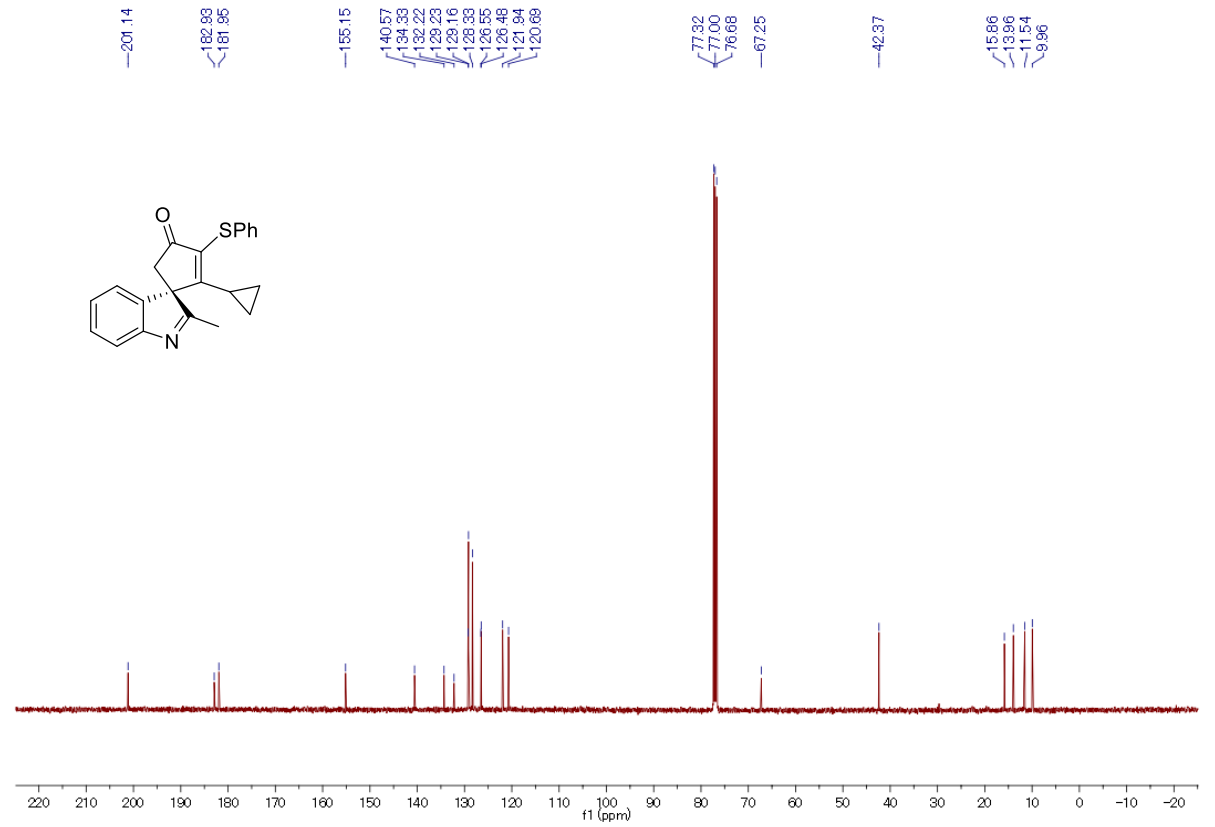
f1 (ppm)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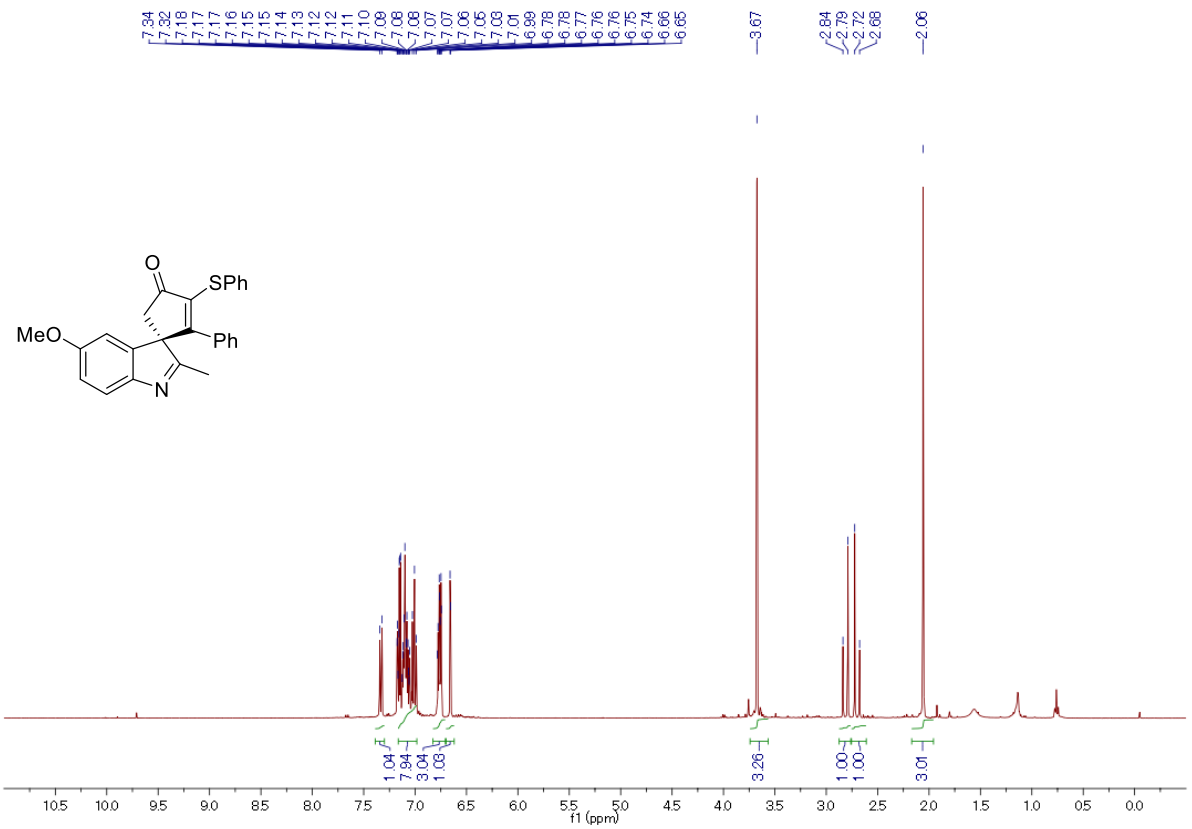
42.37
15.86
13.96
11.54
9.96
O
SPh
N
f1 (ppm)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7.08
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7.08
7.07
7.07
7.06
7.05
7.03
7.01
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6.78
6.78
6.77
6.76
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6.75
6.74
6.66
6.65
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2.79
2.72
2.68
2.06
O
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MeO
Ph
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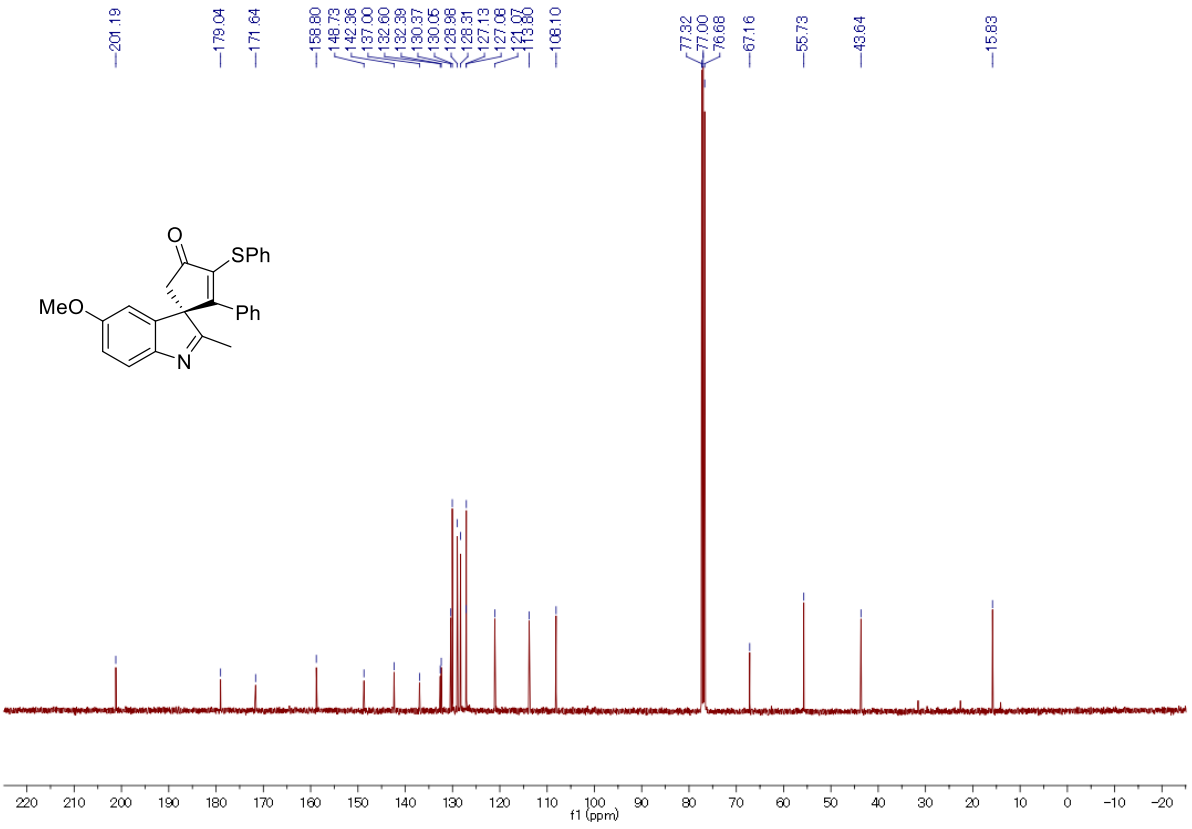
3.01
f1 (ppm)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128.31
127.13
127.08
121.07
113.80
108.10
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55.73
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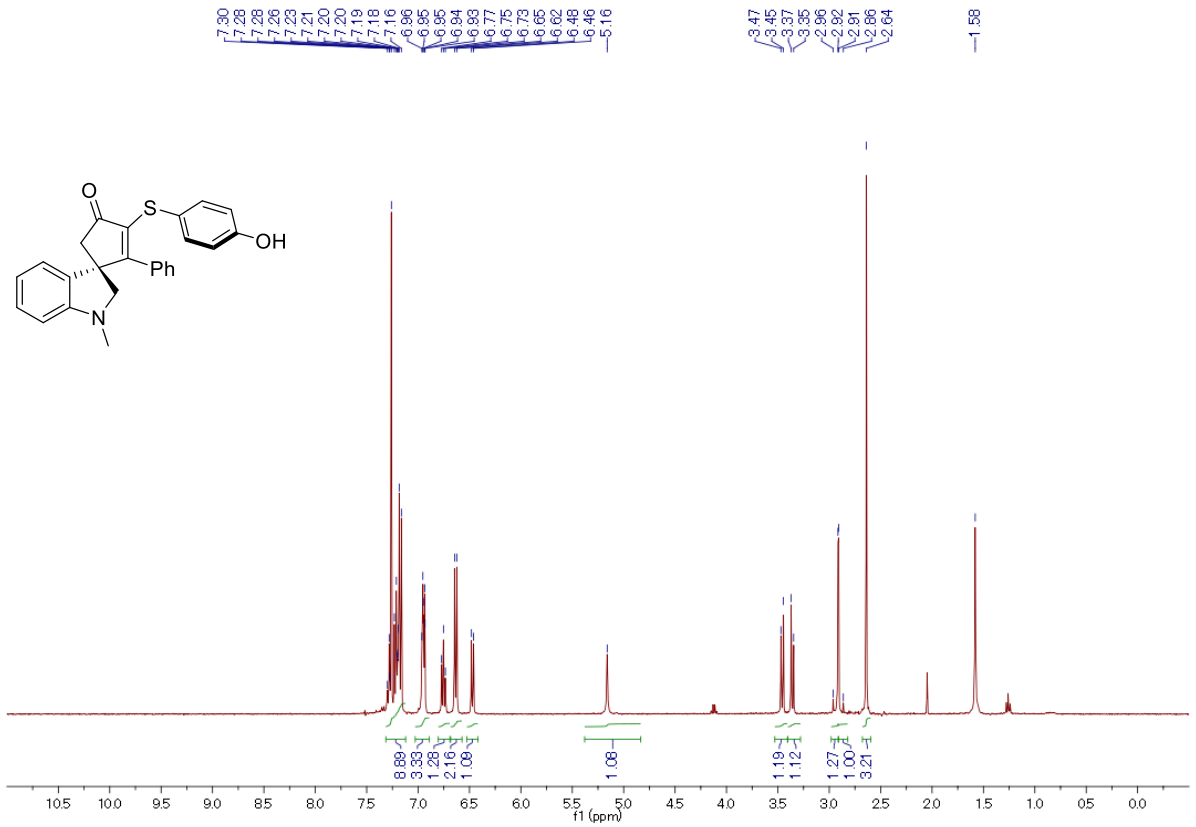
O
SPh
MeO
Ph
N
f1 (ppm)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3.35
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2.91
2.86
2.64
1.58
O
S
OH
Ph
N
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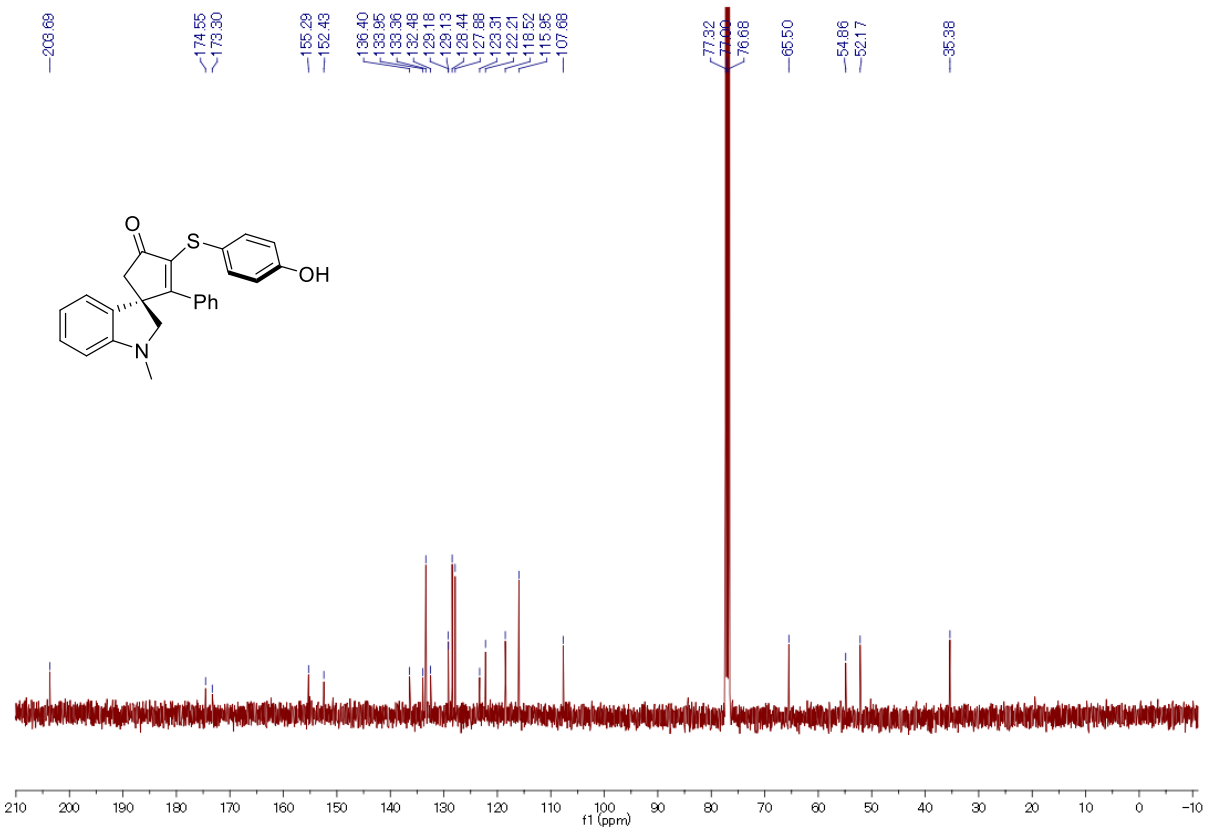
f1 (ppm)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128.44
127.88
123.31
122.21
118.52
115.95
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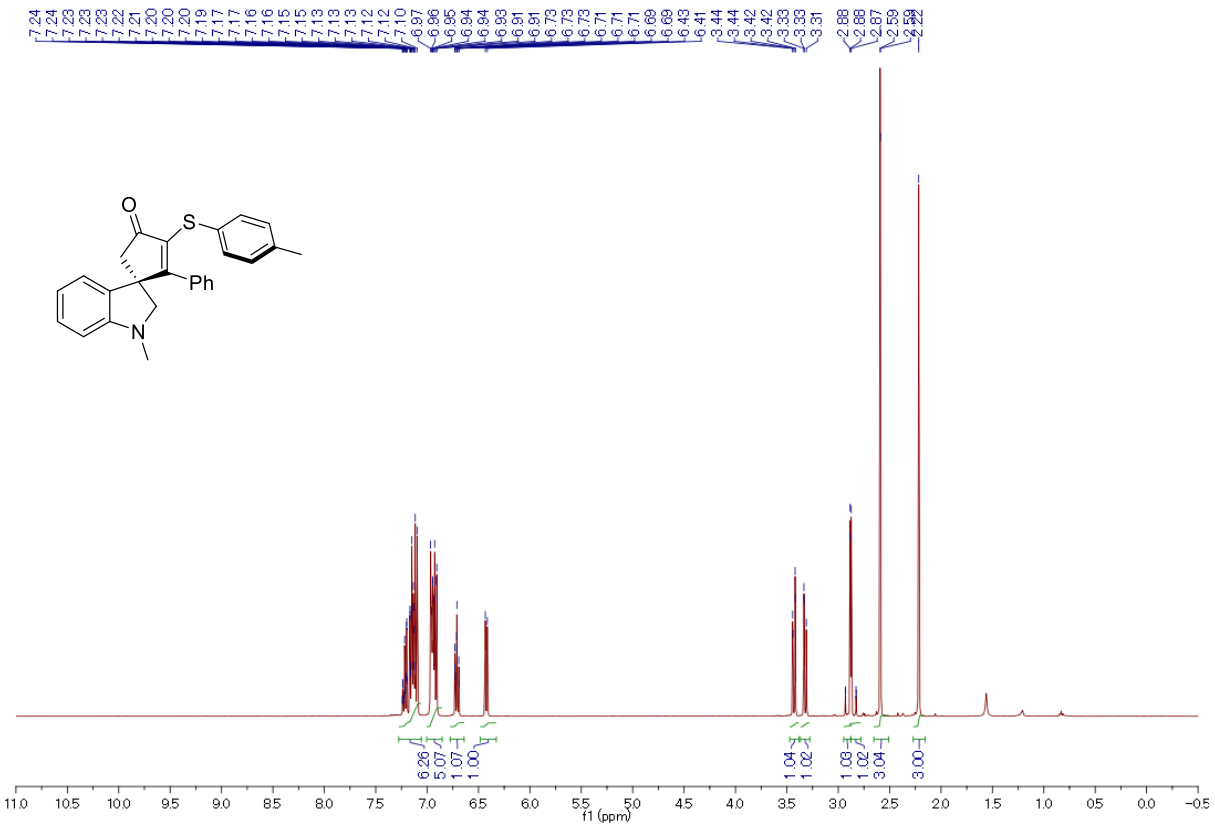
S
OH
Ph
N
f1 (ppm)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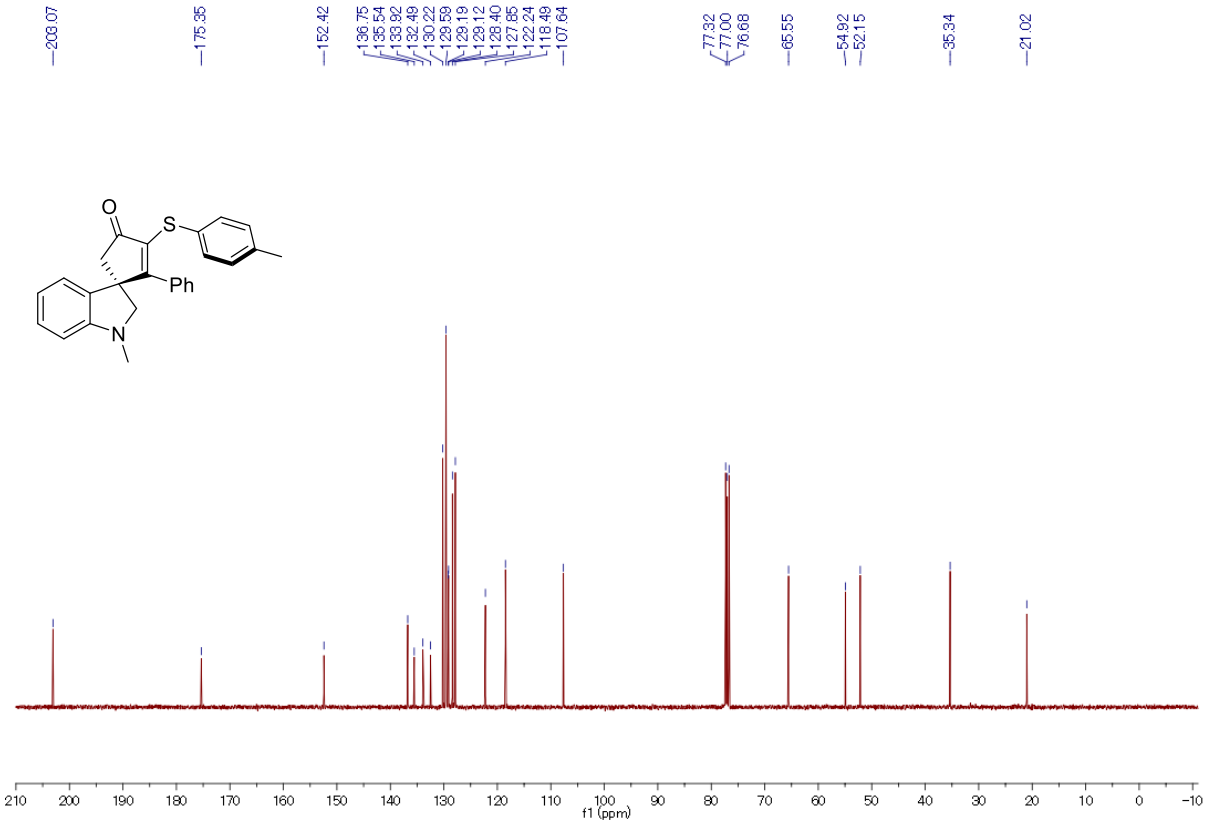
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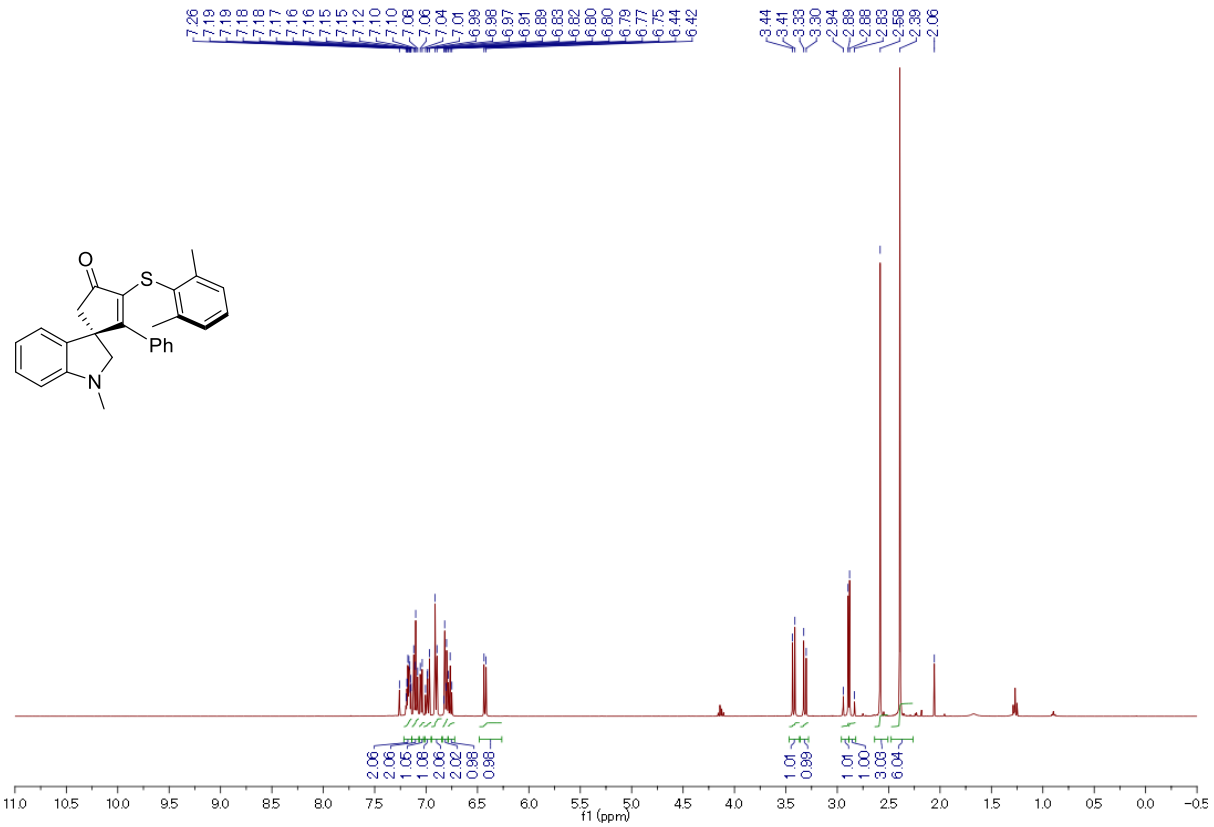
f1 (ppm)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6.82
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6.79
6.77
6.75
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6.42
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3.41
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2.39
2.06
O
S
Ph
N
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2.06
1.05
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1.01
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1.00
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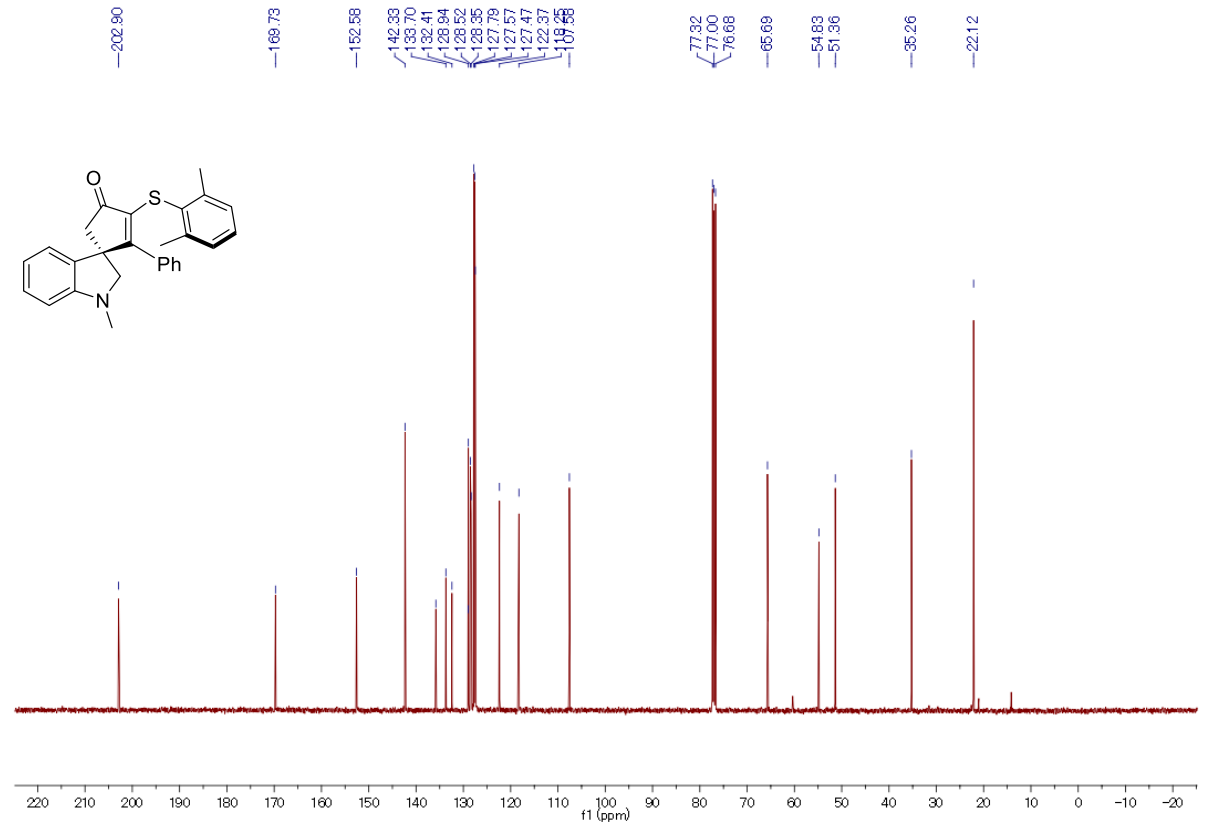
6.04
f1 (ppm)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107.88
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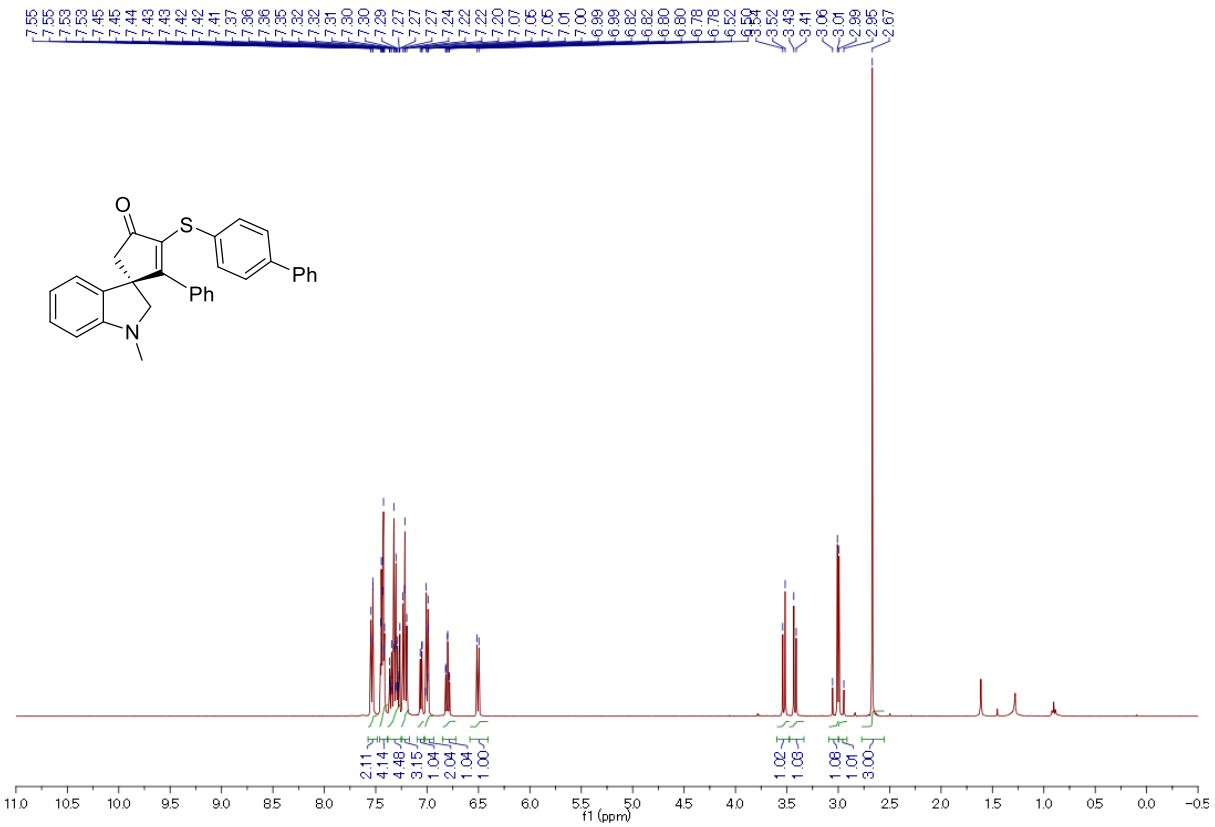
22.12
O
S
Ph
N
f1 (ppm)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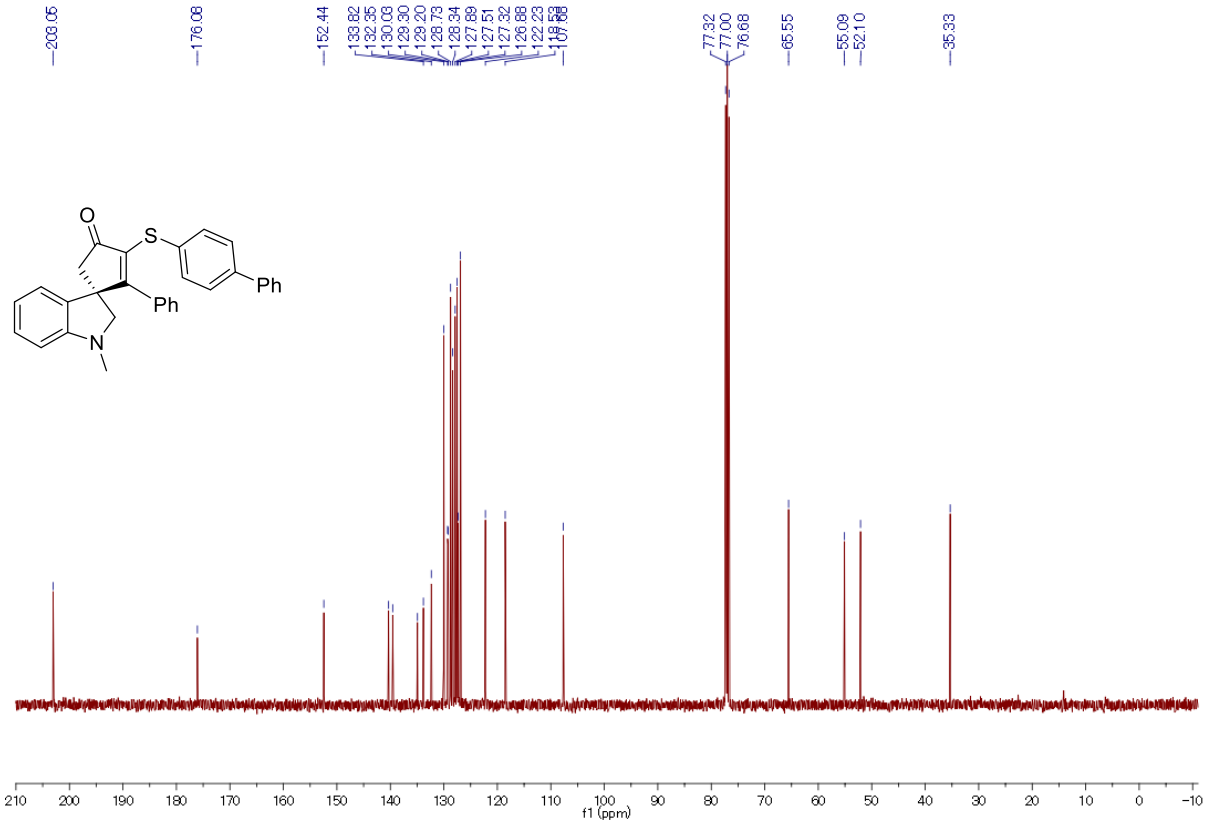
S
Ph
Ph
N
f1 (ppm)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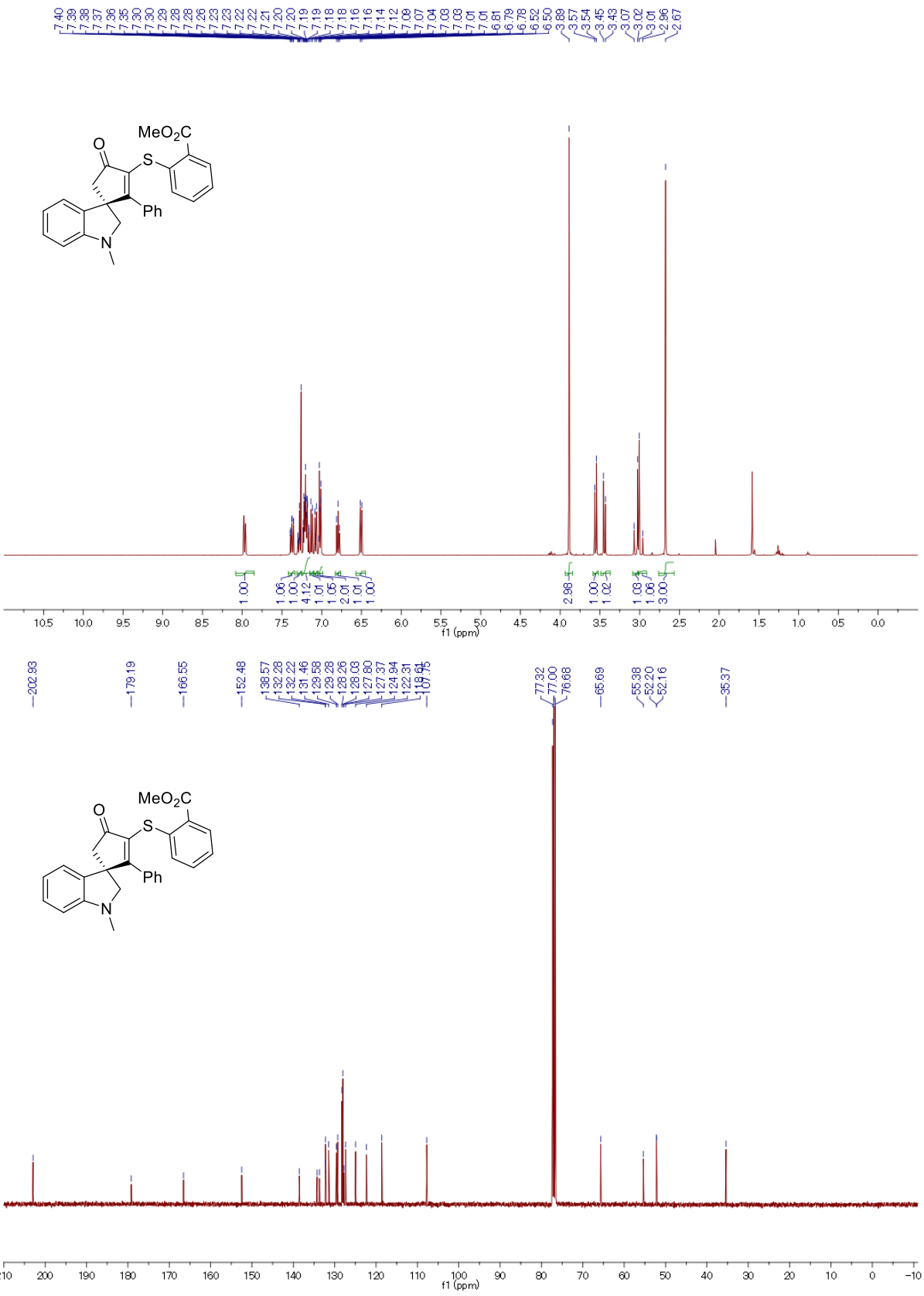
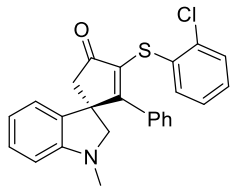
S
Ph
Ph
N
f1 (ppm)


MeO2C
O
S
Ph
N
f1 (ppm)


O
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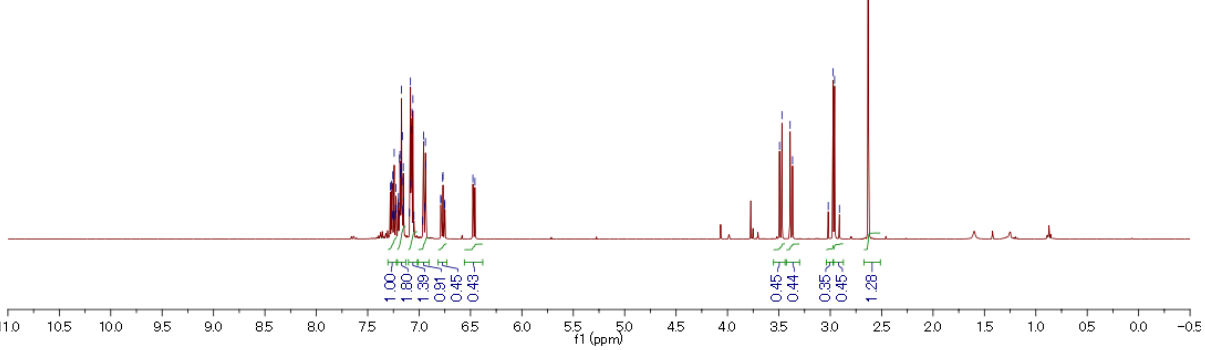
Cl
Ph
N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0.45
0.44
0.35
0.45
1.28
f1 (ppm)


p7677jre
JRashont 608/1/P
175.91
152.66
133.83
132.34
132.18
131.30
129.94
129.49
129.35
128.24
128.06
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126.99
122.60
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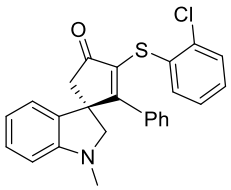
77.16
76.84
65.82
55.37
52.05
35.50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Ph
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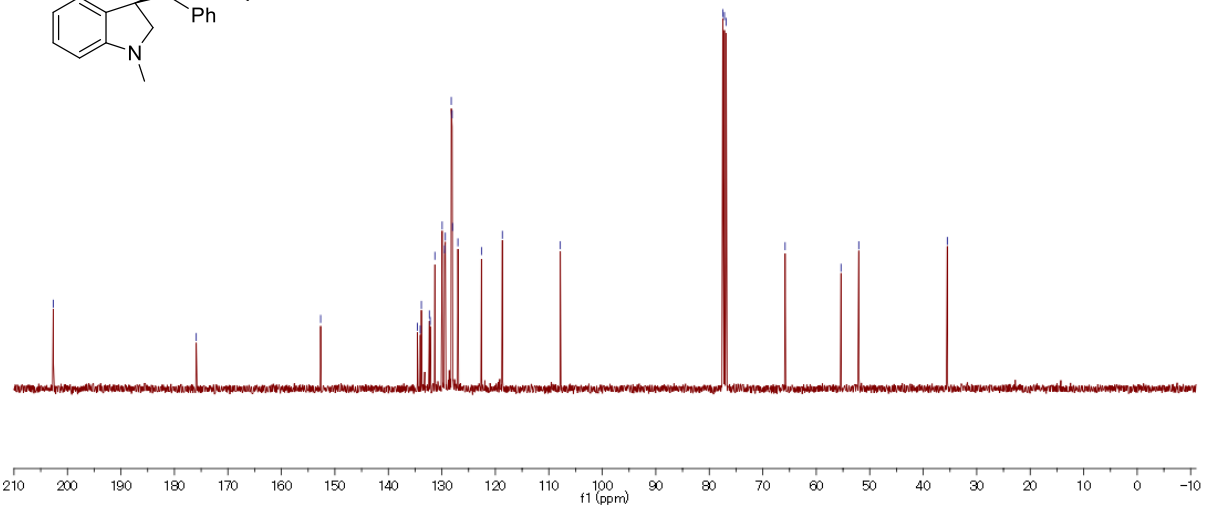
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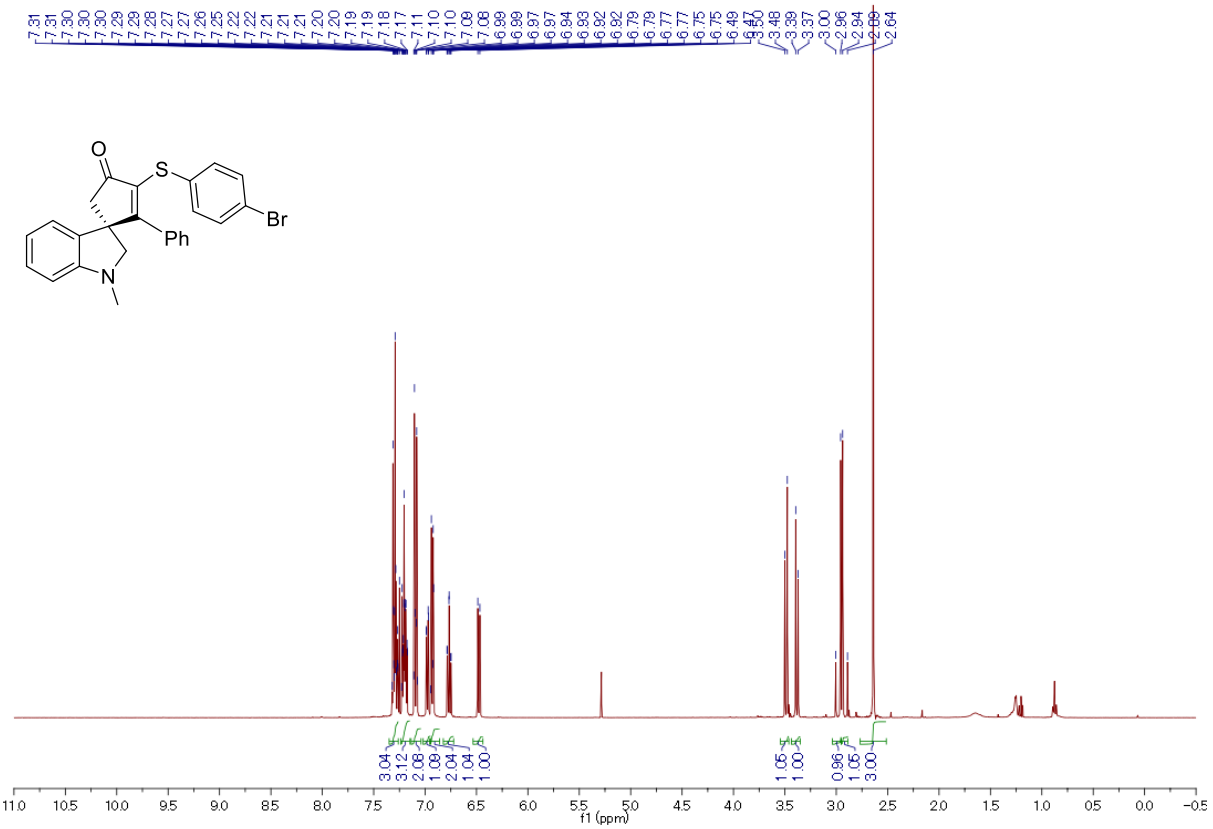
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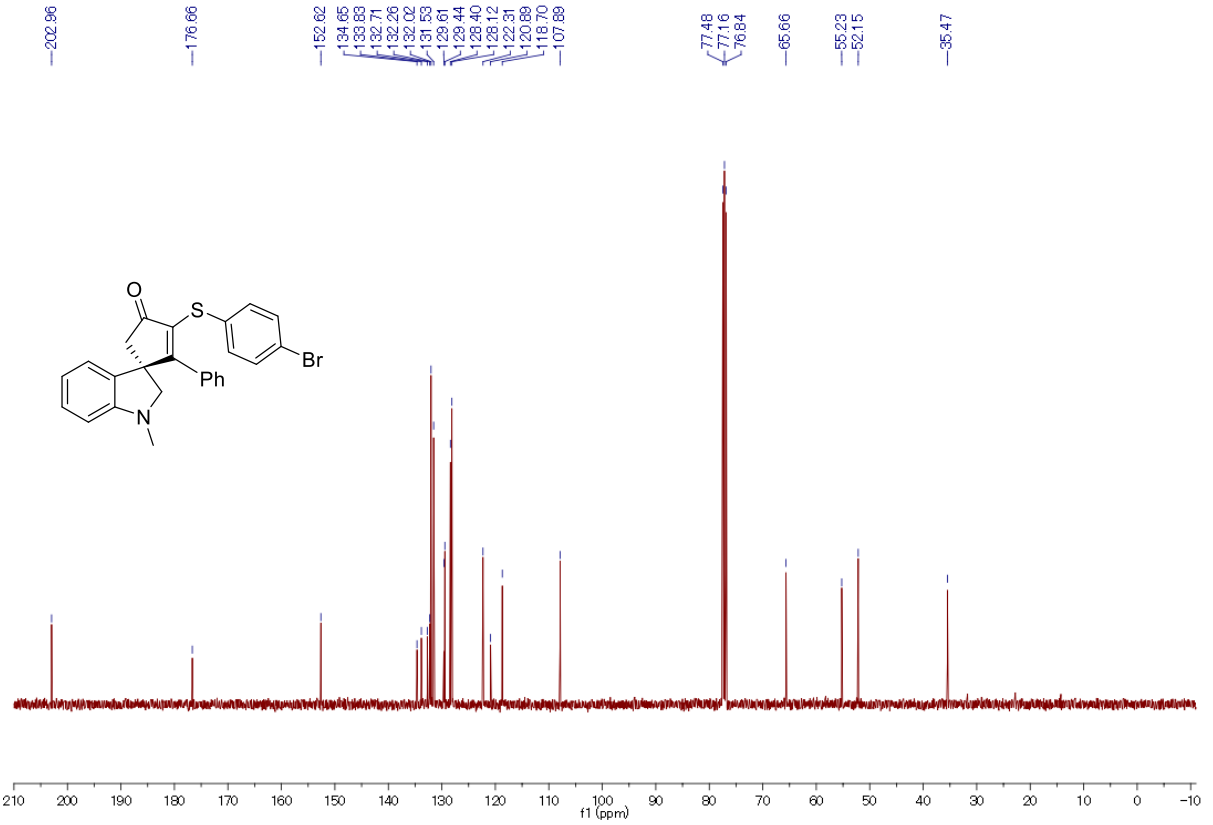
S
Br
Ph
N
f1 (ppm)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Ph
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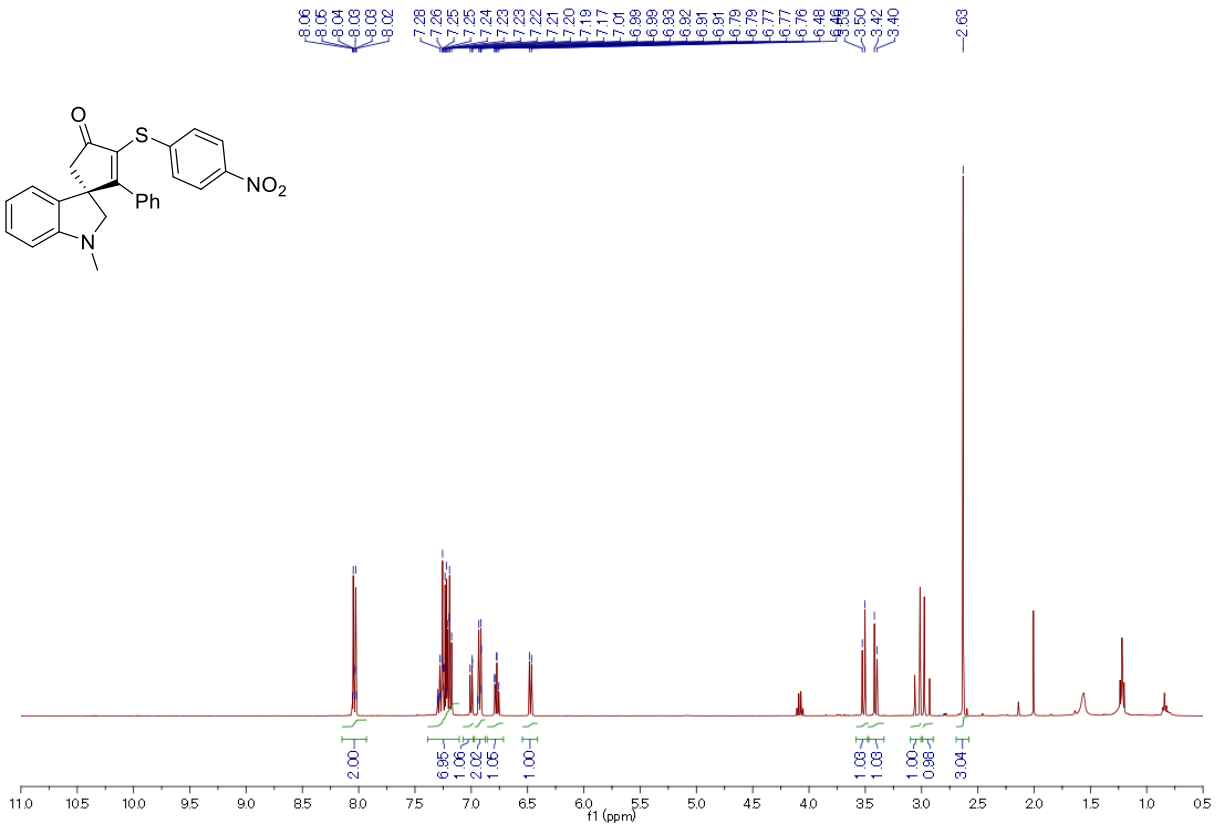
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7.17
7.01
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6.99
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6.92
6.91
6.91
6.79
6.79
6.77
6.77
6.76
6.48
3.50
3.42
3.40
2.63
O
S
NO2
Ph
N
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1.00
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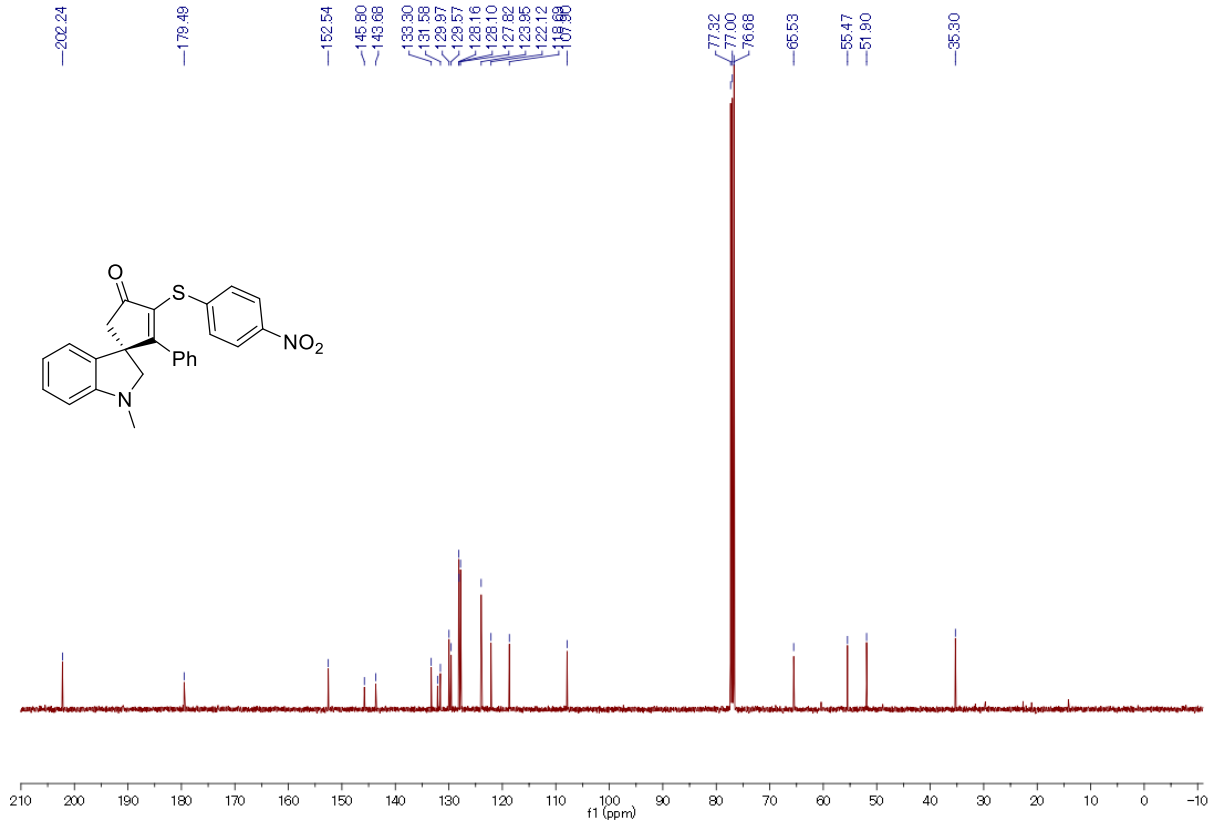
3.04
f1 (ppm)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O
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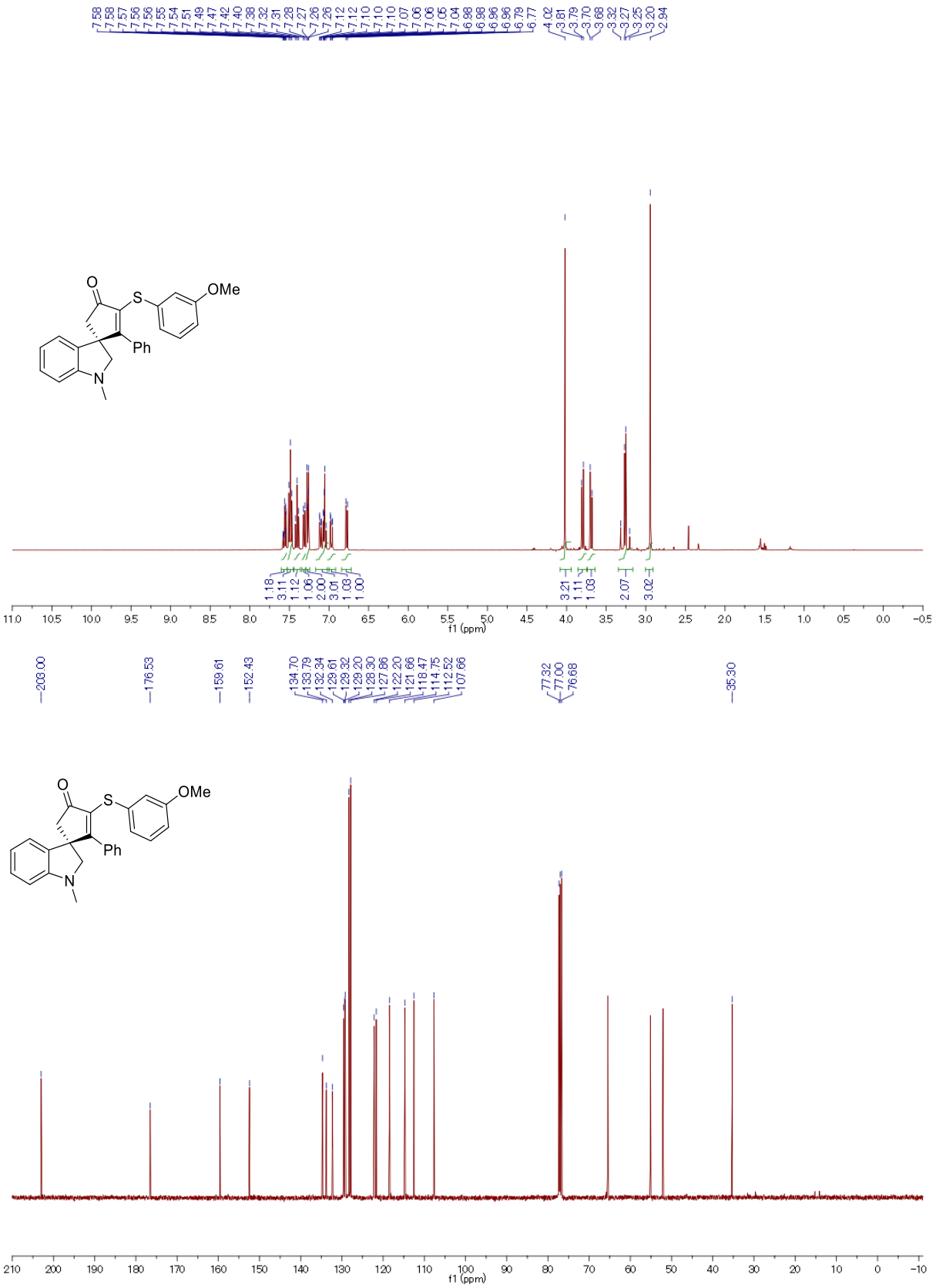
Ph
N
f1 (ppm)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7.10
7.10
7.10
7.07
7.06
7.06
7.05
7.04
6.98
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6.96
6.96
6.79
6.77
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3.81
3.79
3.70
3.68
3.32
3.27
3.25
3.20
2.94
O
S
OMe
Ph
N
1.18
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1.12
1.06
2.00
3.01
1.09
1.00
3.21
1.11
1.03
2.07
3.02
f1 (ppm)
208.00
176.53
159.61
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128.30
127.86
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O
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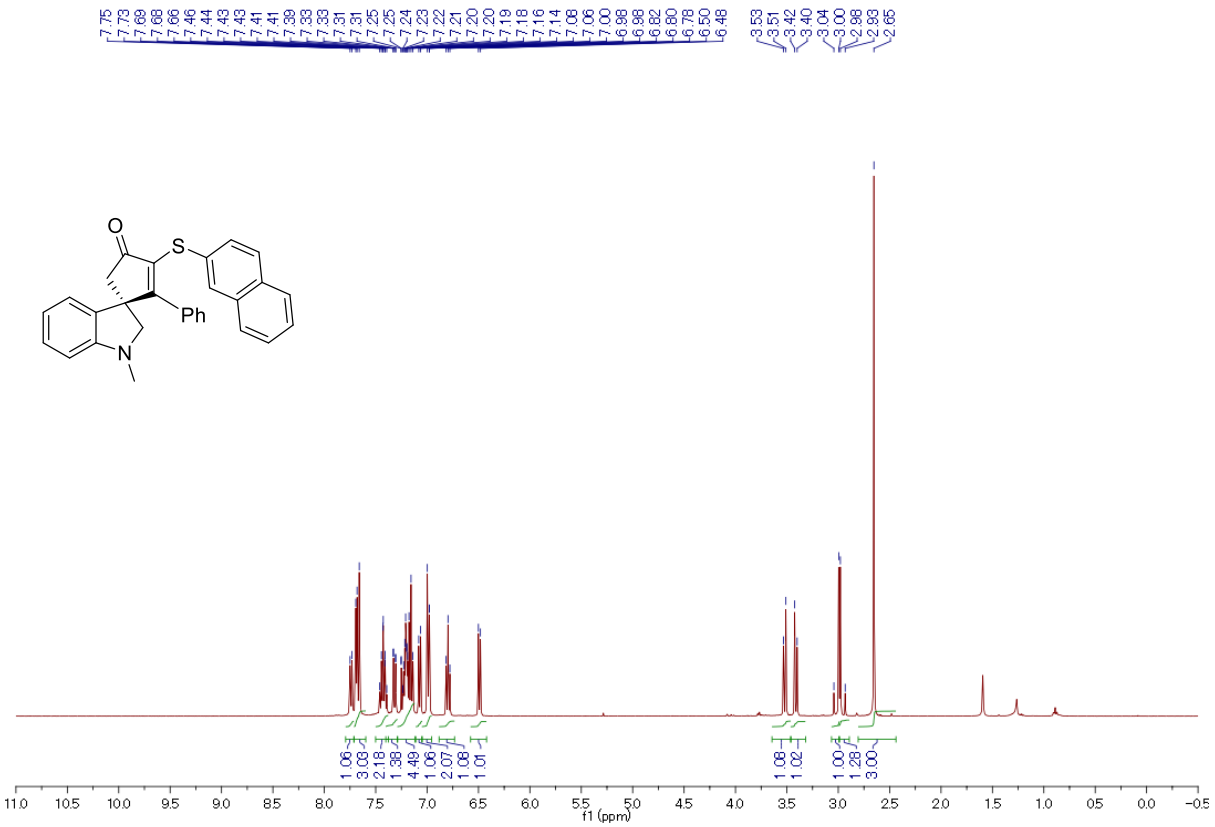
OMe
Ph
N
f1 (ppm)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7.18
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7.14
7.06
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6.50
6.48
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3.51
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3.00
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O
S
Ph
N
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1.02
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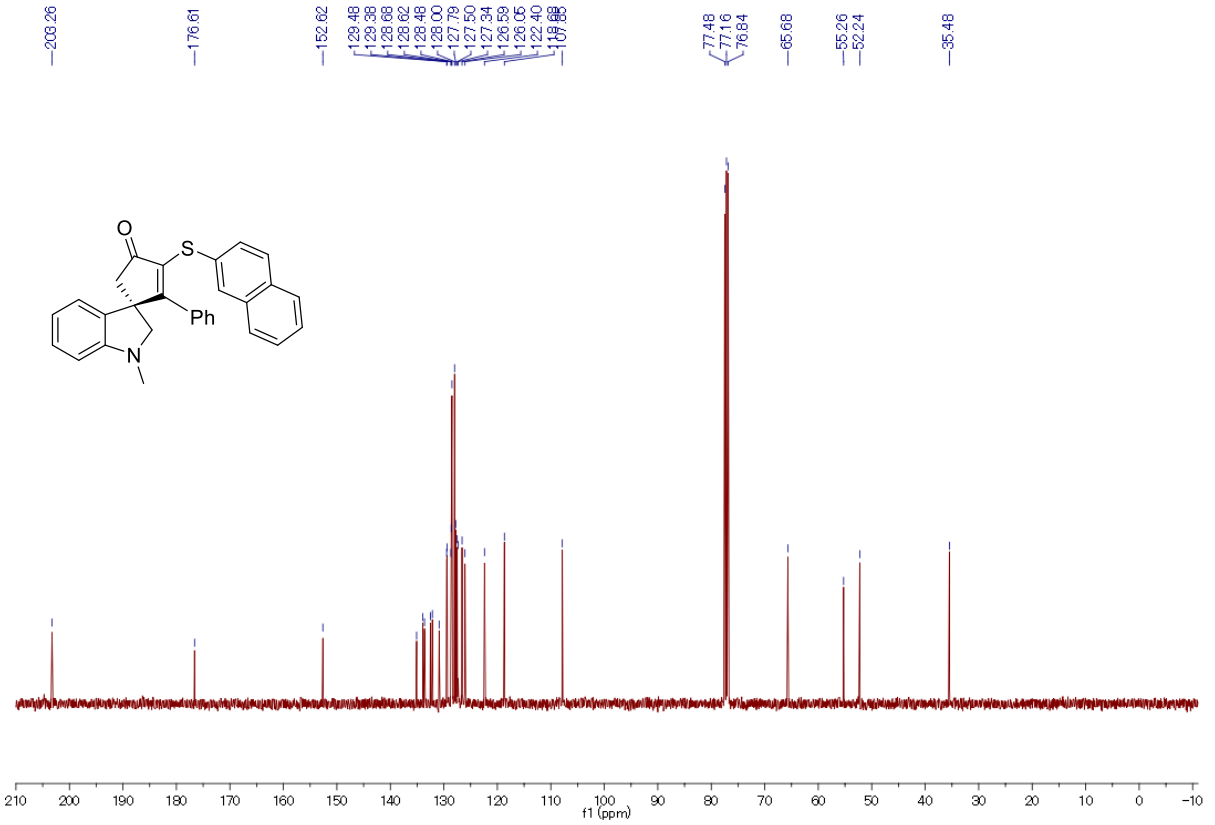
3.00
f1 (ppm)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122.40
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76.84
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55.26
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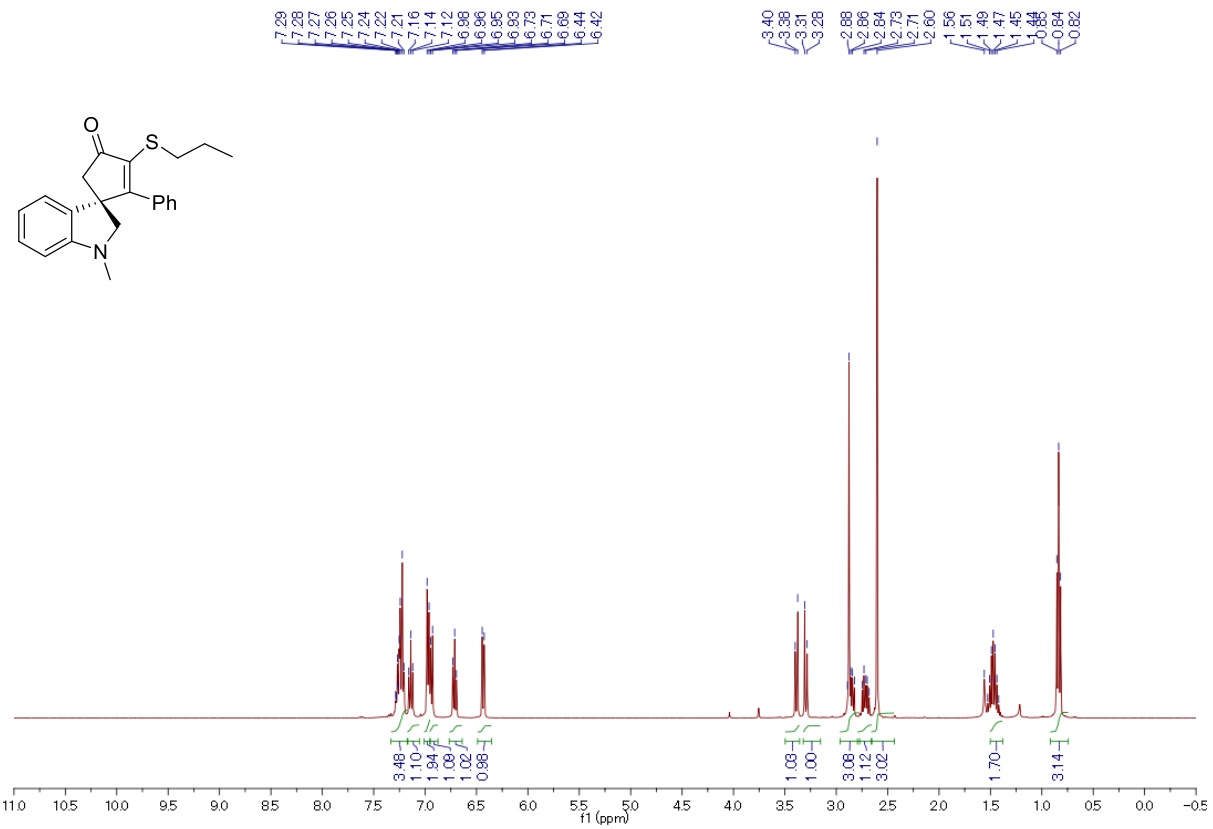
35.48
O
S
Ph
N
f1 (ppm)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0.82
O
S
Ph
N
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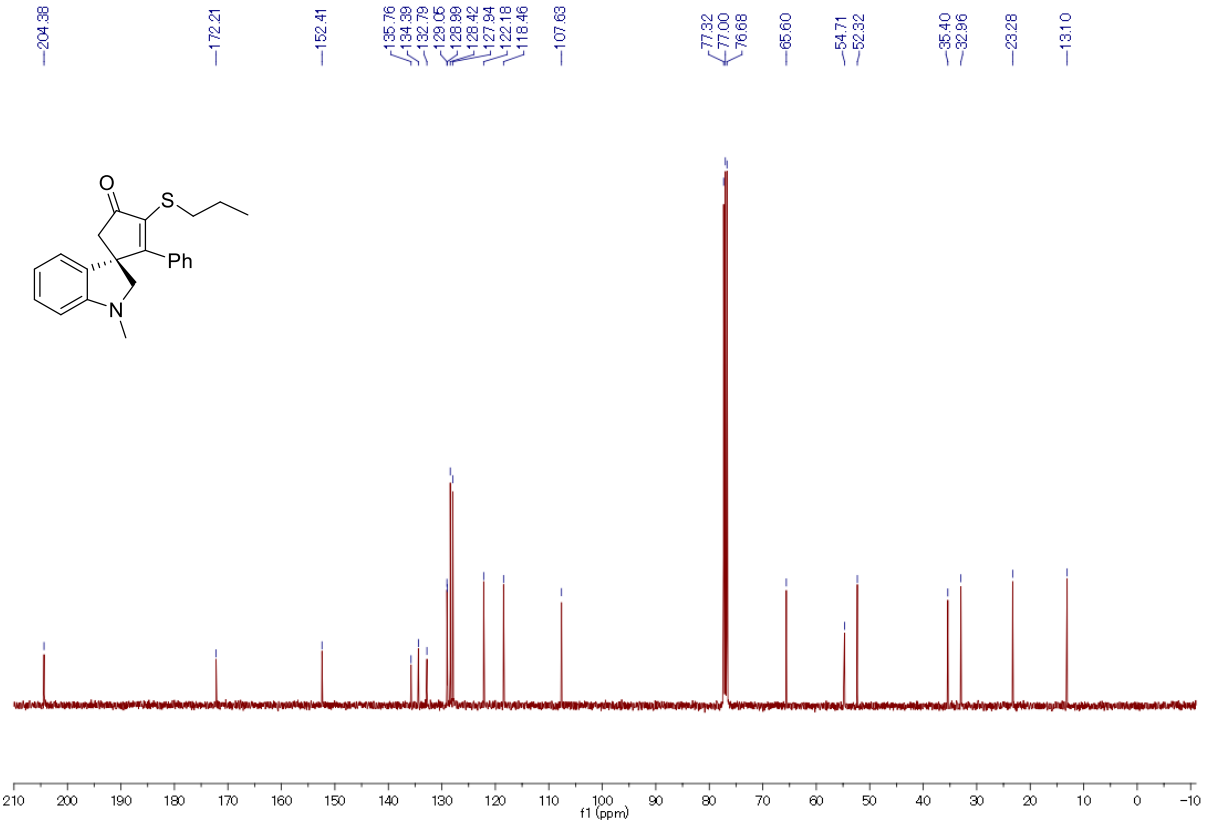
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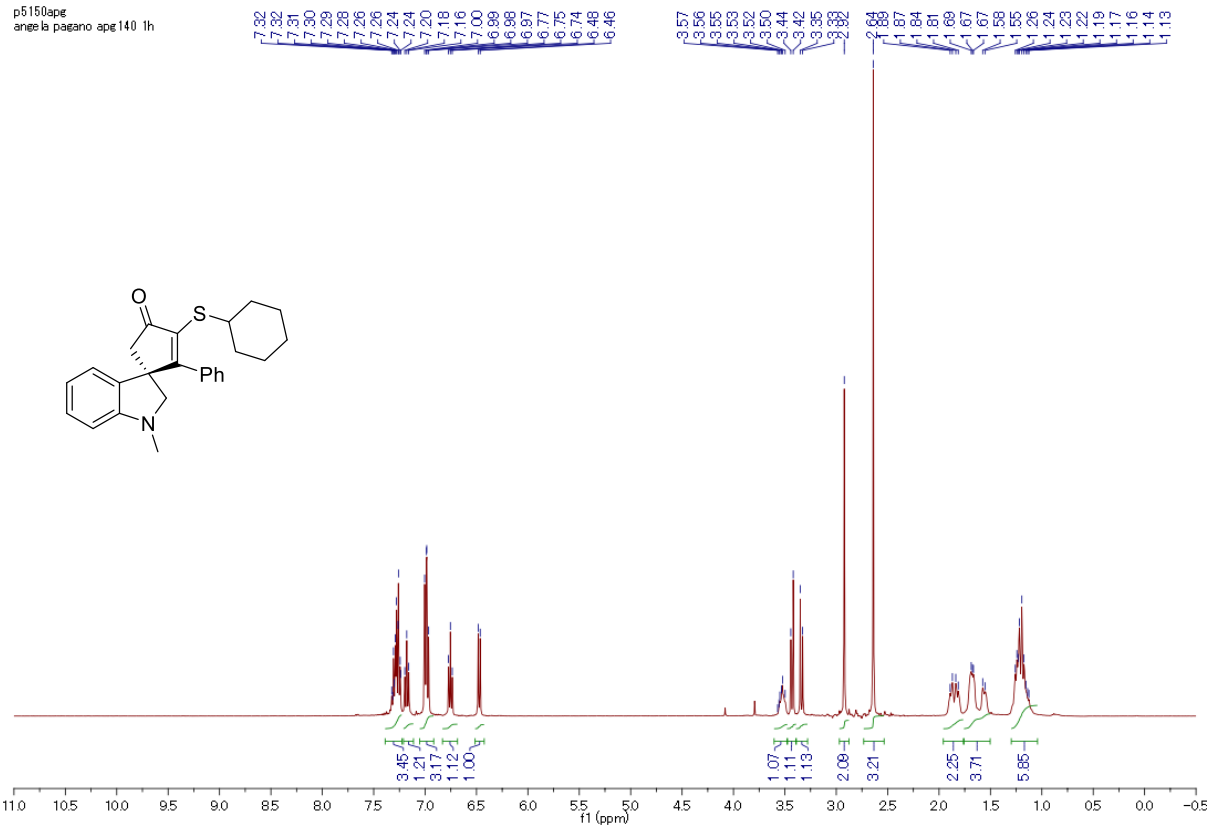
23.28
13.10
O
S
Ph
N
f1 (ppm)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angela pagano apg140 1h
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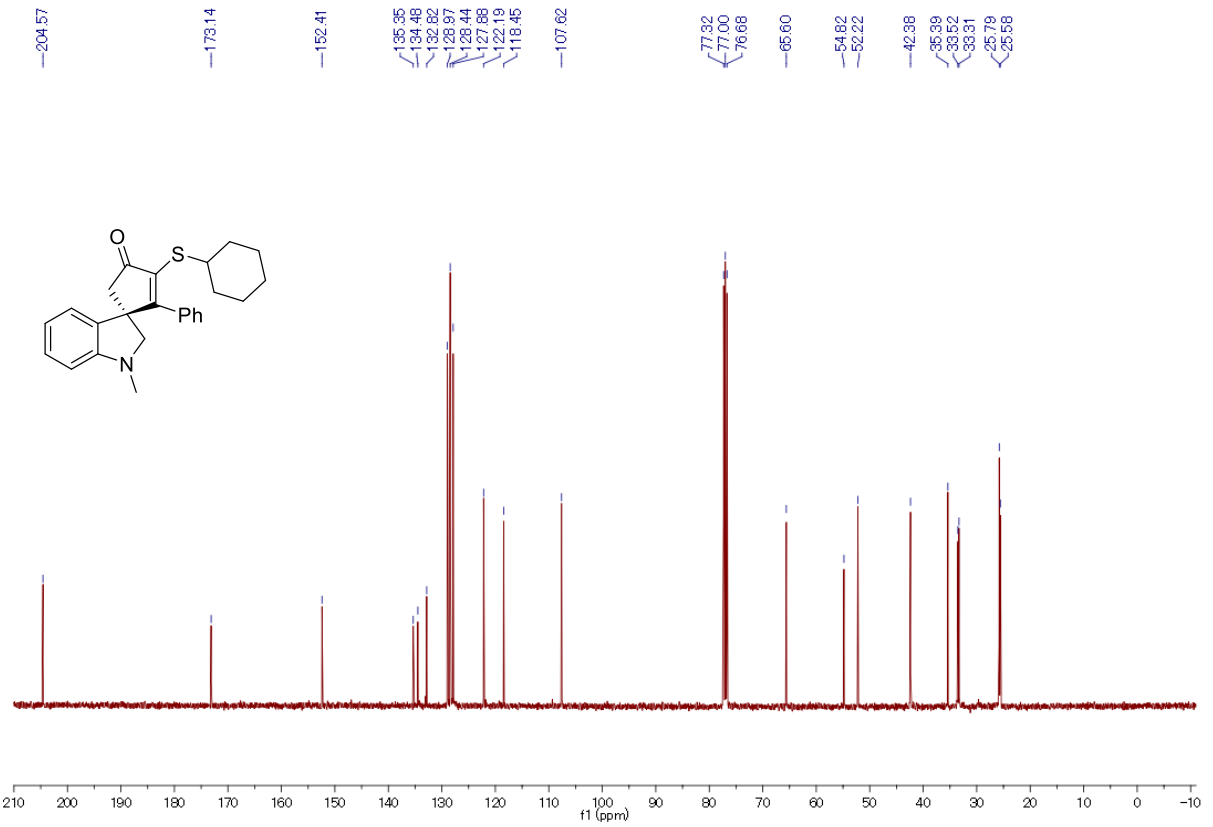
S
Ph
N
f1 (ppm)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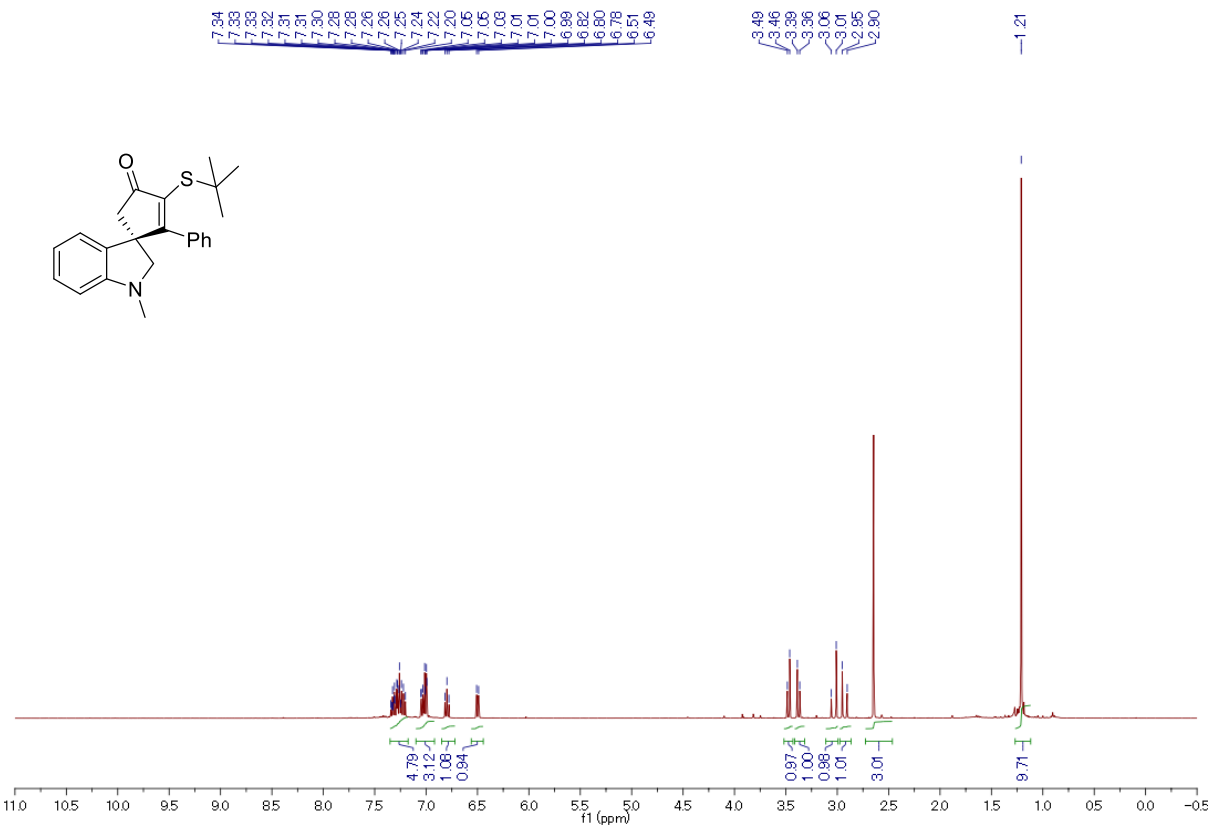
f1 (ppm)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7.05
7.03
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7.01
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6.51
6.49
3.49
3.46
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3.36
3.06
3.01
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2.90
1.21
O
S
Ph
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1.01
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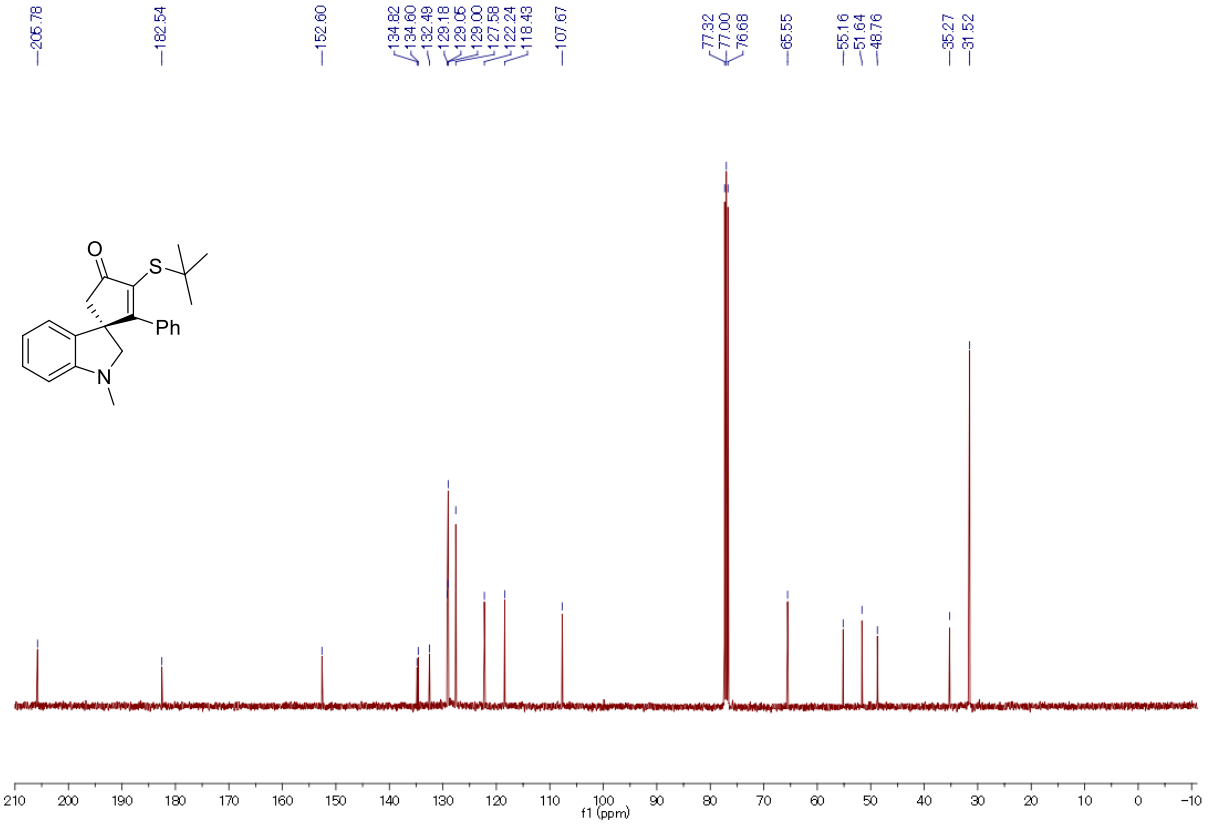
9.71
f1 (ppm)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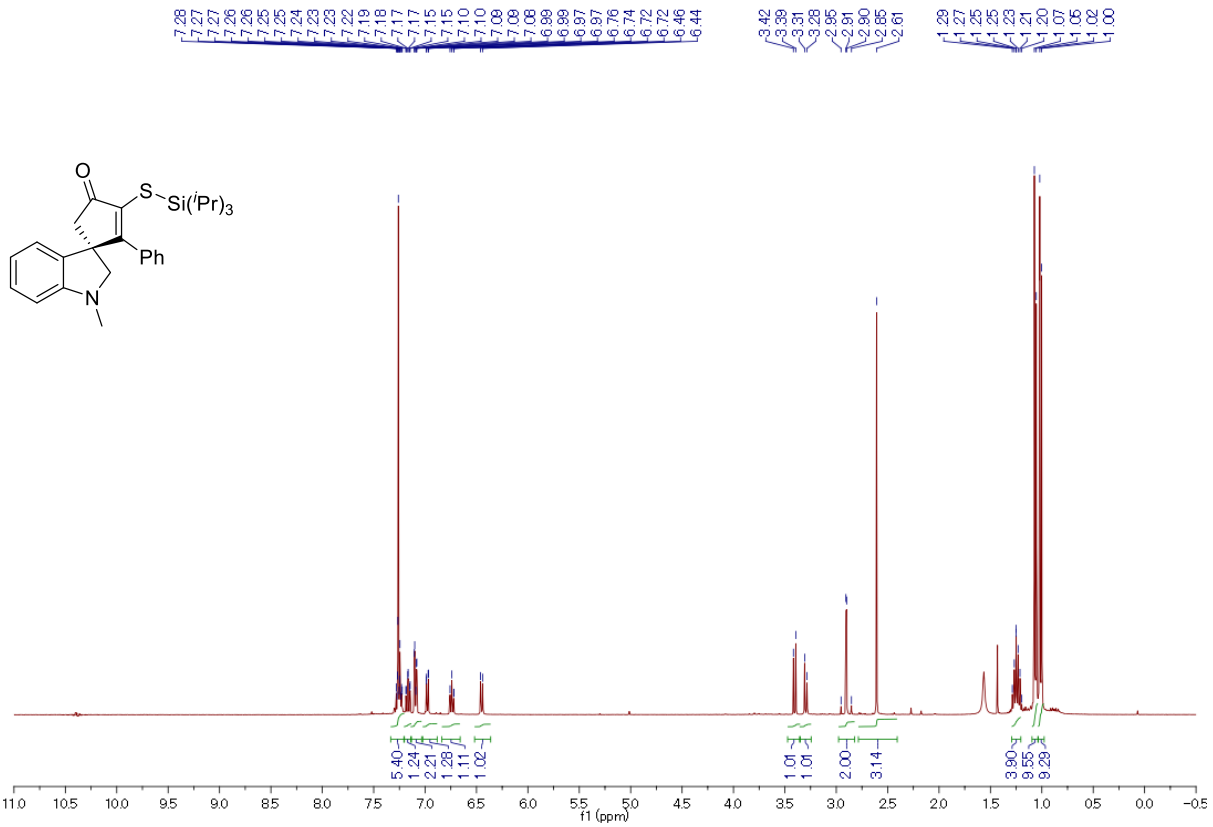
31.52
O
S
Ph
N
f1 (ppm)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7.08
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3.39
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2.85
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1.27
1.25
1.25
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1.05
1.02
1.00
O
S
Si(iPr)3
Ph
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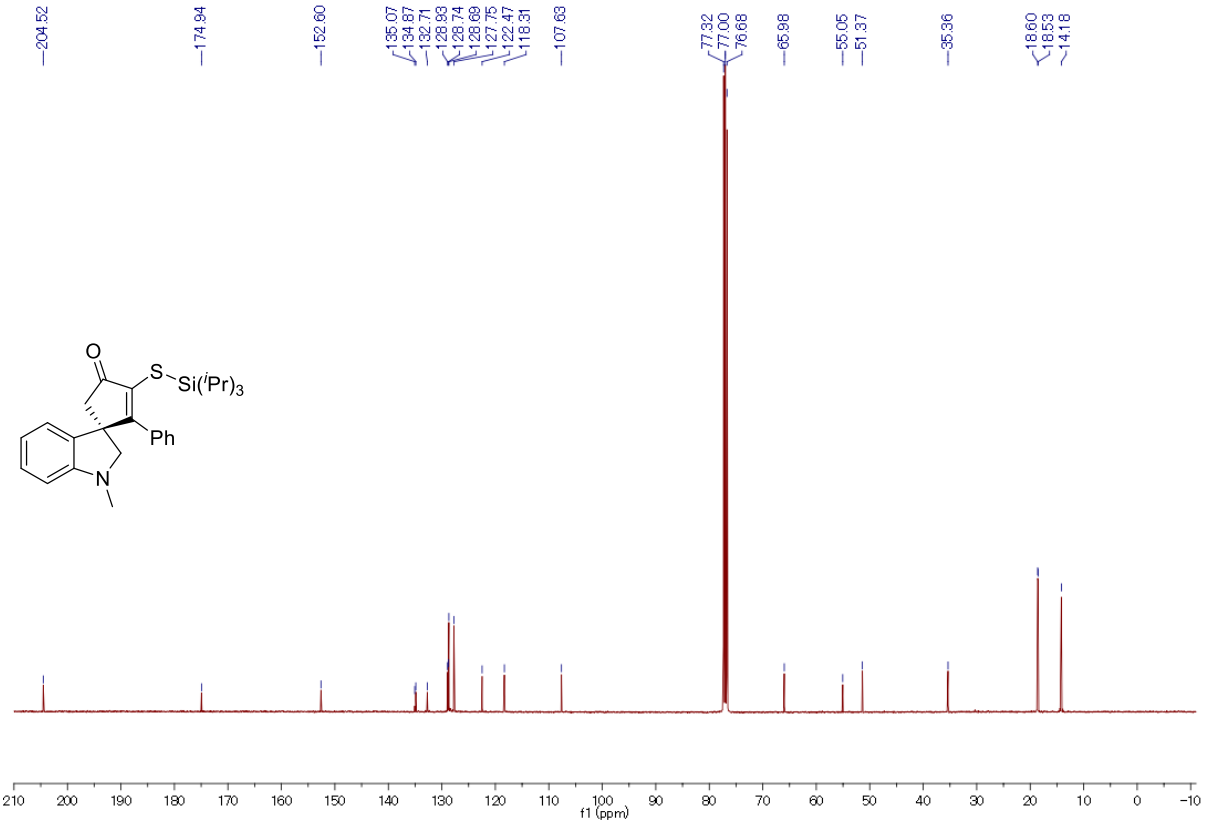
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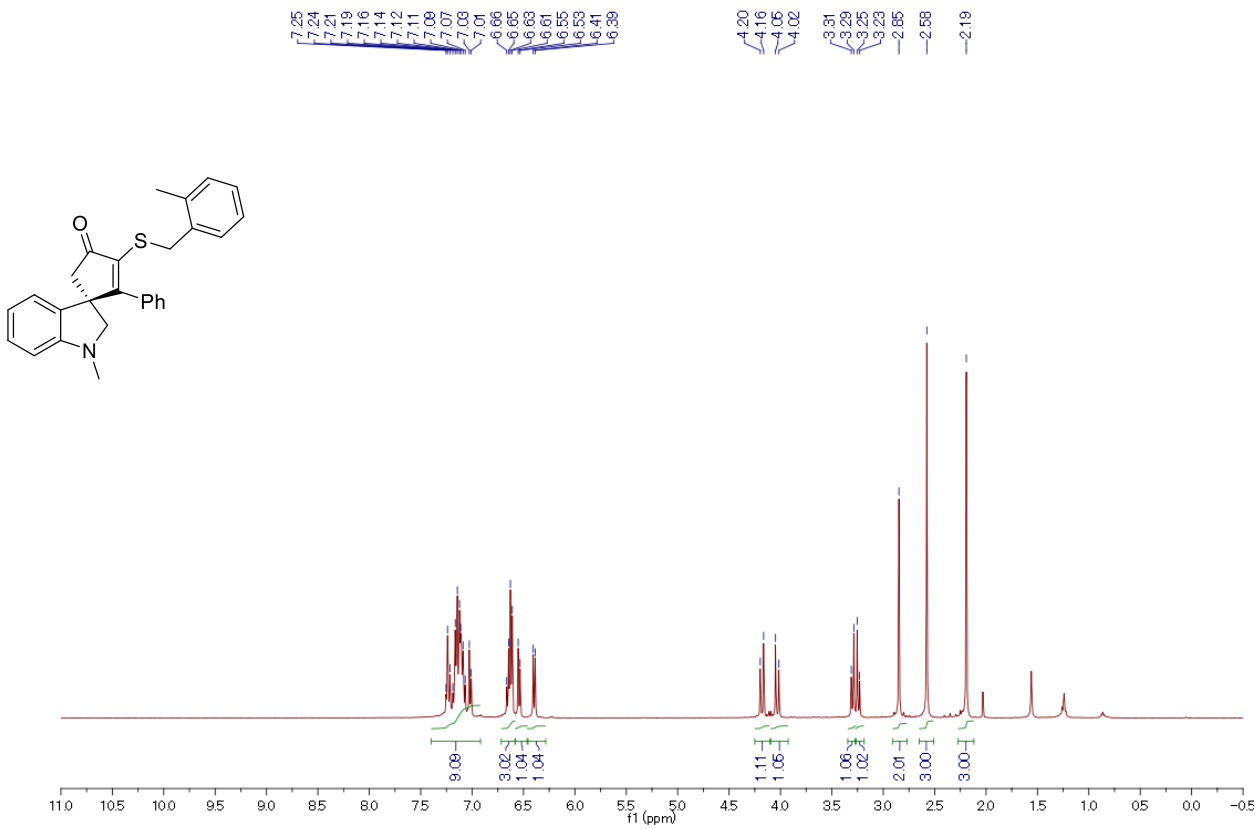
18.53
14.18
O
S
Si(iPr)3
Ph
N
f1 (ppm)


7.25
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7.11
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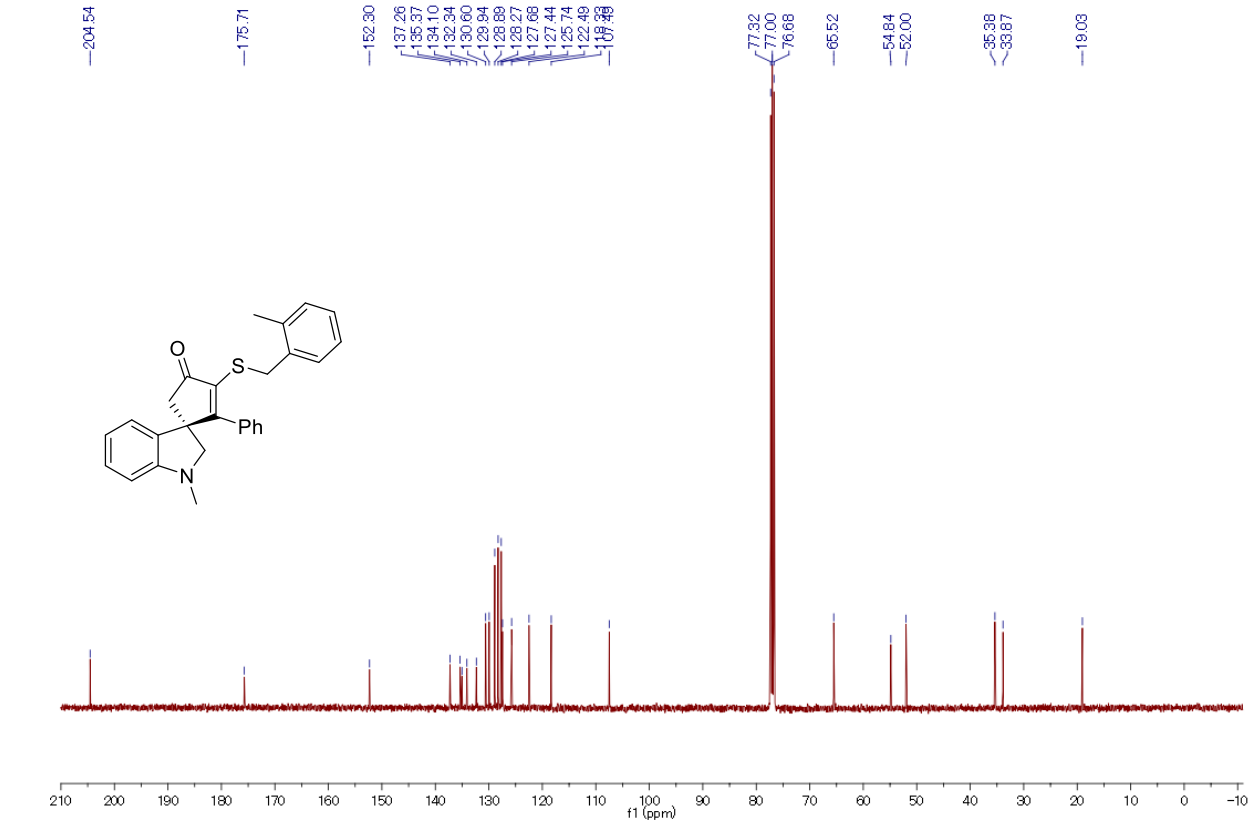
7.07
7.03
7.01
6.66
6.65
6.63
6.61
6.55
6.53
6.41
6.39
4.20
4.16
4.05
4.02
3.31
3.29
3.25
3.23
2.85
2.58
2.19
O
S
Ph
N
9.08
3.02
1.04
1.04
1.11
1.05
1.06
1.02
2.01
3.00
3.00
f1 (ppm)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134.10
132.34
130.60
129.94
128.89
128.27
127.68
127.44
125.74
122.49
77.32
77.00
76.68
65.52
54.84
52.00
35.38
33.87
19.03
O
S
Ph
N
f1 (ppm)


7.28
7.27
7.27
7.25
7.25
7.24
7.24
7.23
7.22
7.22
7.21
7.20
7.19
7.18
7.15
7.15
7.13
7.13
7.11
7.11
6.98
6.96
6.94
6.93
6.93
6.92
6.92
6.91
6.73
6.71
6.69
6.43
6.41
3.56
3.39
3.37
3.30
3.27
3.22
3.20
3.19
3.17
3.15
3.08
3.06
3.06
3.05
3.05
3.03
3.01
2.92
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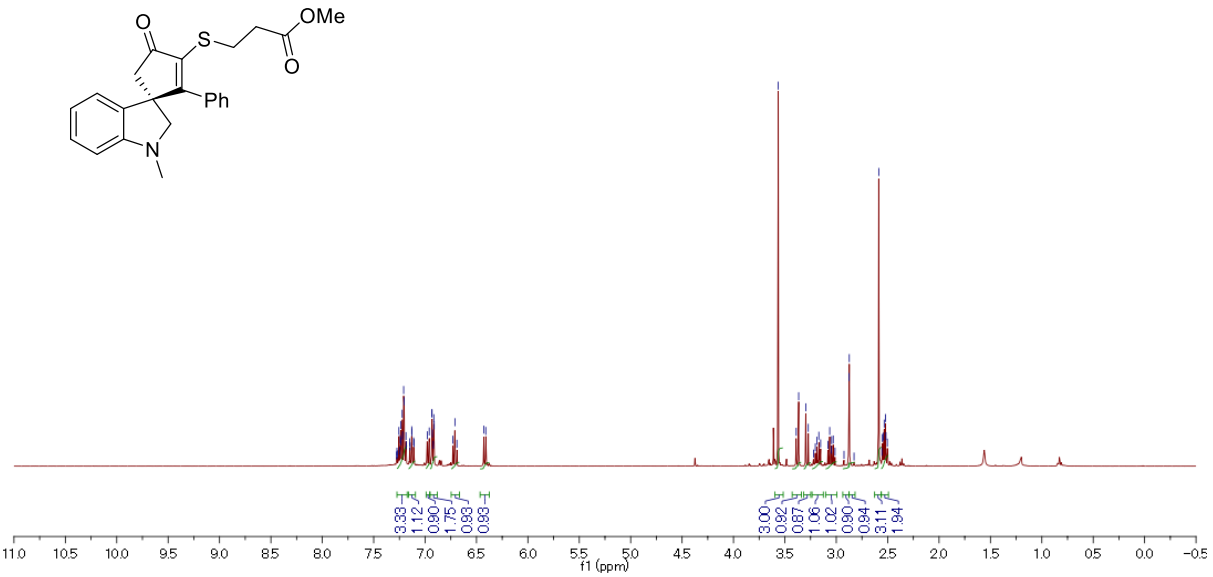
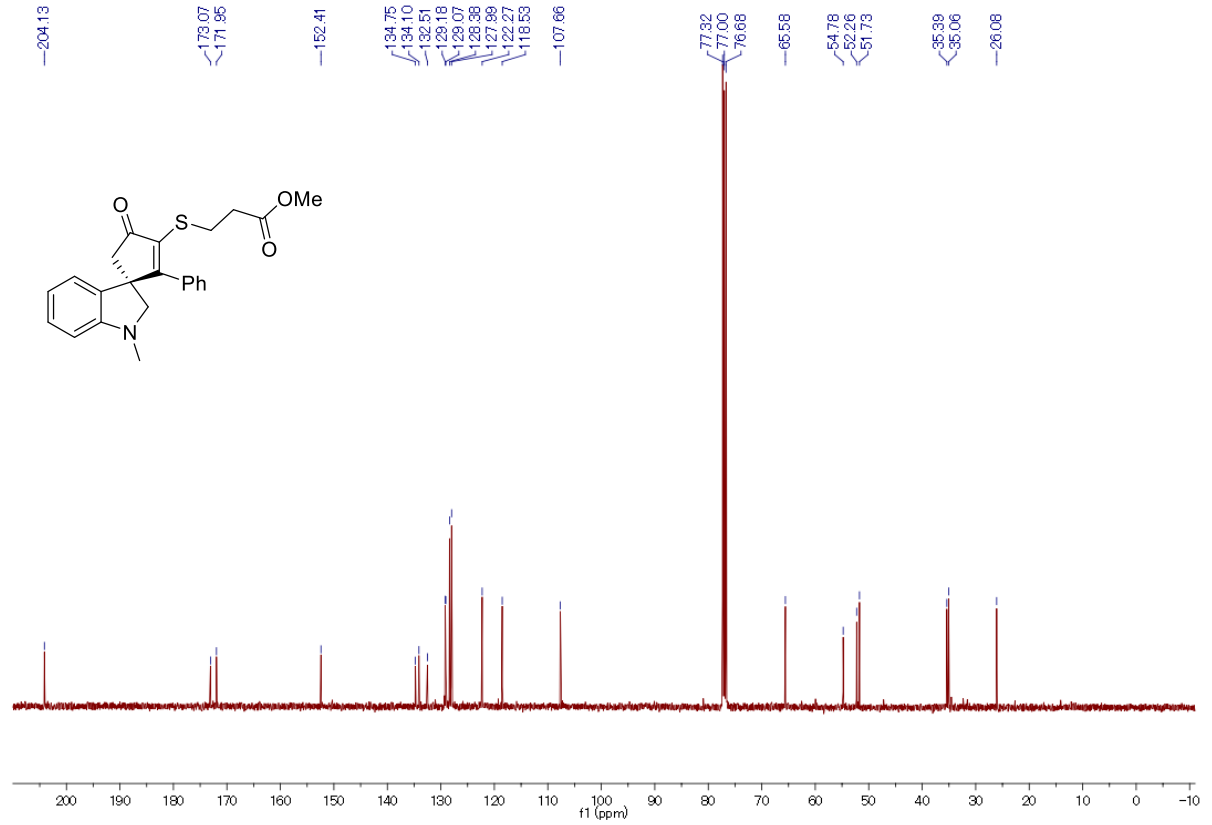
2.87
2.83
2.59
2.56
2.55
2.54
2.53
2.52
2.52
2.50


O
S
OMe
O
Ph
N
3.33
1.12
0.90
1.75
0.93
0.93
3.00
0.92
0.87
1.06
1.02
0.90
0.94
3.11
1.94
f1 (ppm)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173.07
171.95
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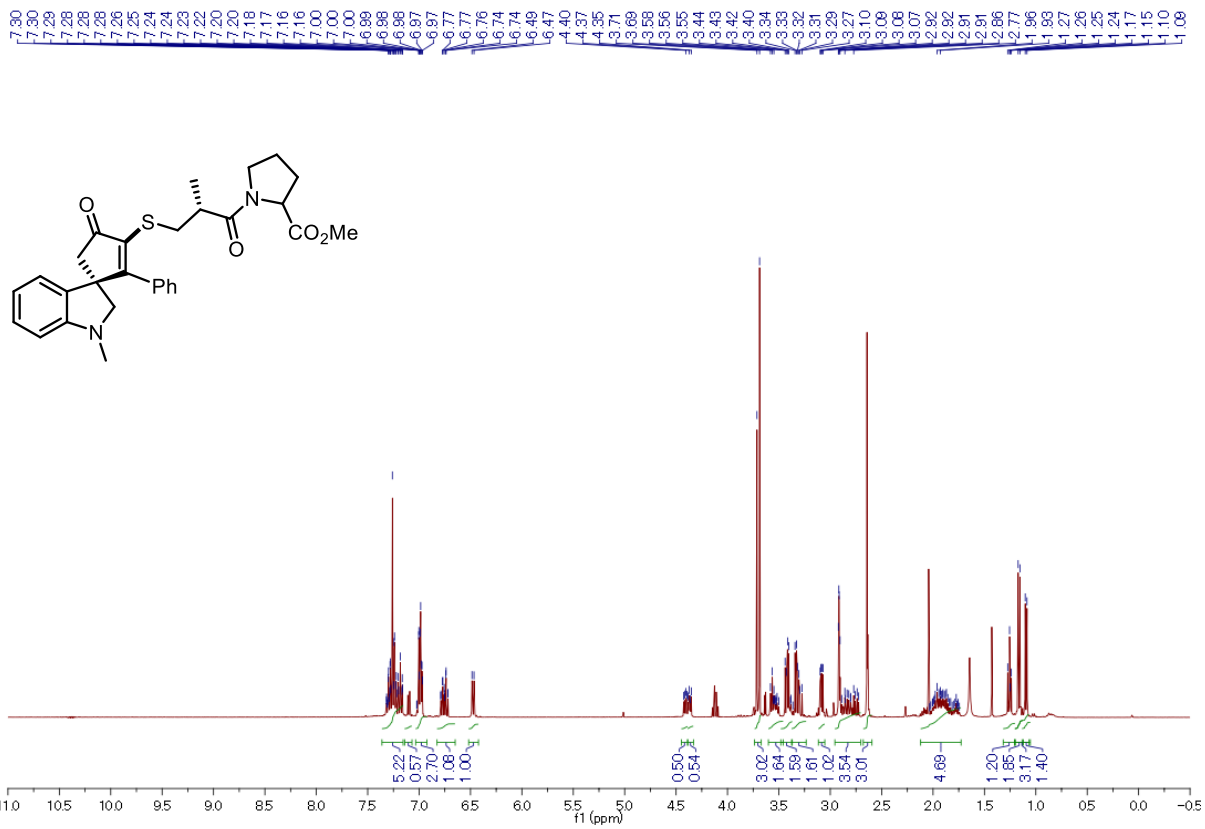
134.75
134.10
132.51
129.18
129.07
128.38
127.99
122.27
118.53
107.66
77.32
77.00
76.68
65.58
54.78
52.26
51.73
35.39
35.06
26.08
O
S
OMe
O
Ph
N
f1 (ppm)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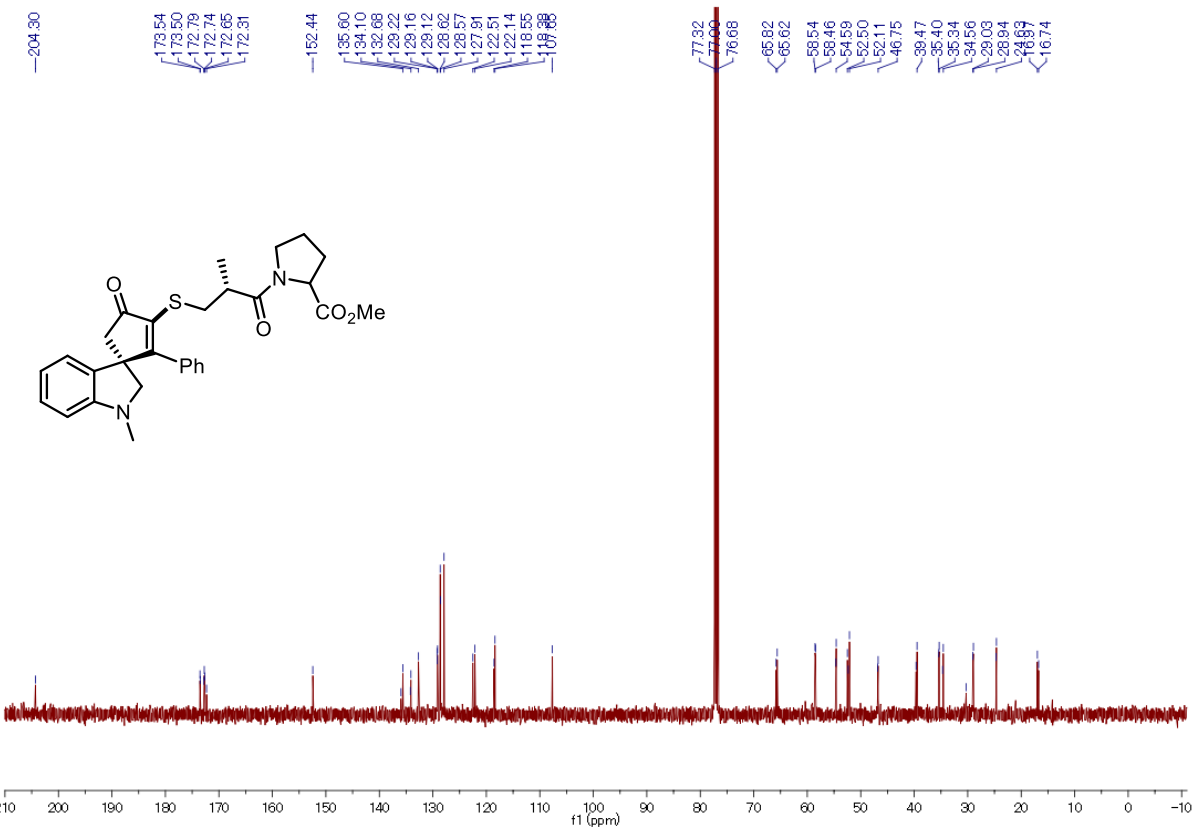
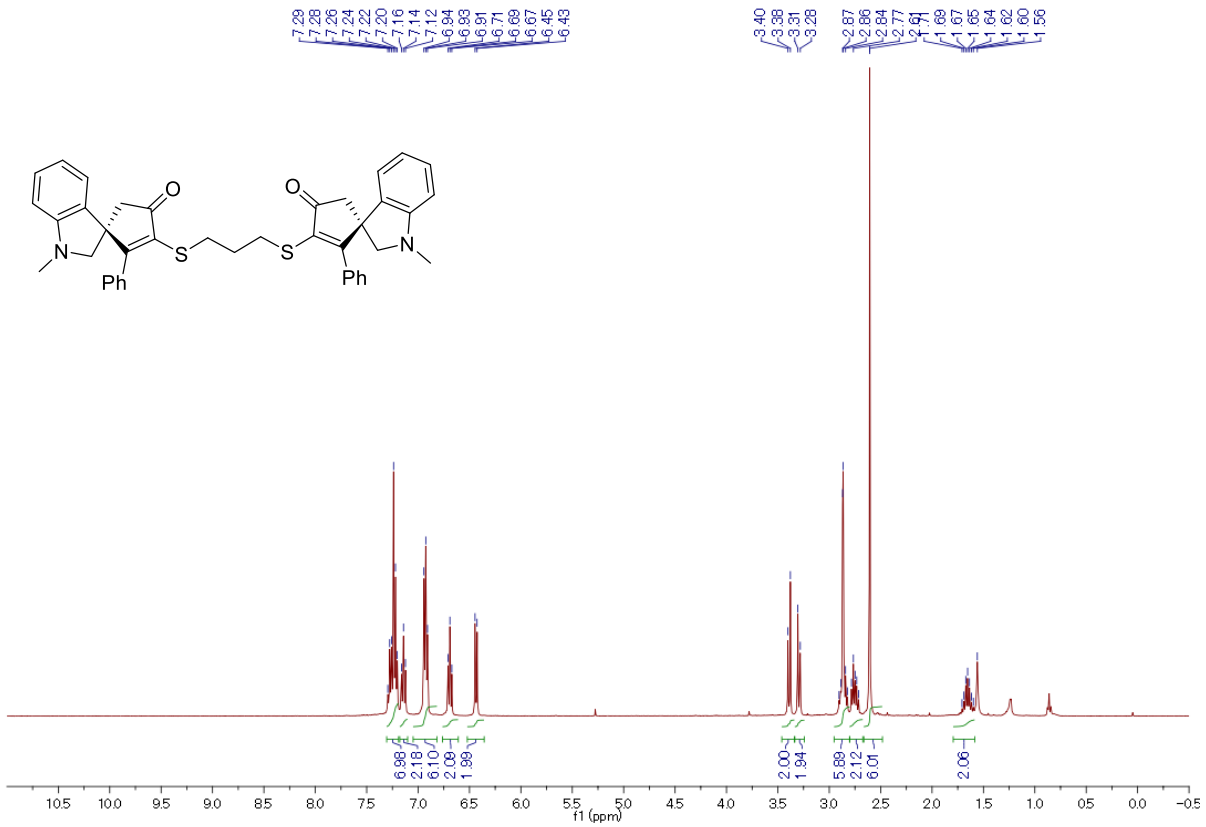
O
S
N
O
CO2Me
Ph
N
5.22 0.57 2.70 1.08 1.00 0.50 0.54 3.02 1.64 1.59 1.61 1.02 3.54 3.01 4.69 1.20 1.85 3.17 1.40
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


204.30
173.54 173.50 172.79 172.74 172.65 172.31 152.44 135.60 134.10 132.68 129.22 129.16 129.12 128.62 128.57 127.91 122.51 122.14 118.55 118.38 107.88 77.32 77.00 76.68 65.82 65.62 58.54 58.46 54.59 52.50 52.11 46.75 39.47 35.40 35.34 34.56 29.03 28.94 24.69 24.67 16.97 16.74
O
S
N
O
CO2Me
Ph
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.29
7.28
7.26
7.24
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7.20
7.16
7.14
7.12
6.94
6.83
6.91
6.71
6.69
6.67
6.45
6.43
3.40
3.38
3.31
3.28
2.87
2.86
2.84
2.77
2.61
1.71
1.69
1.67
1.65
1.64
1.62
1.60
1.56
O
O
S
S
N
N
Ph
Ph
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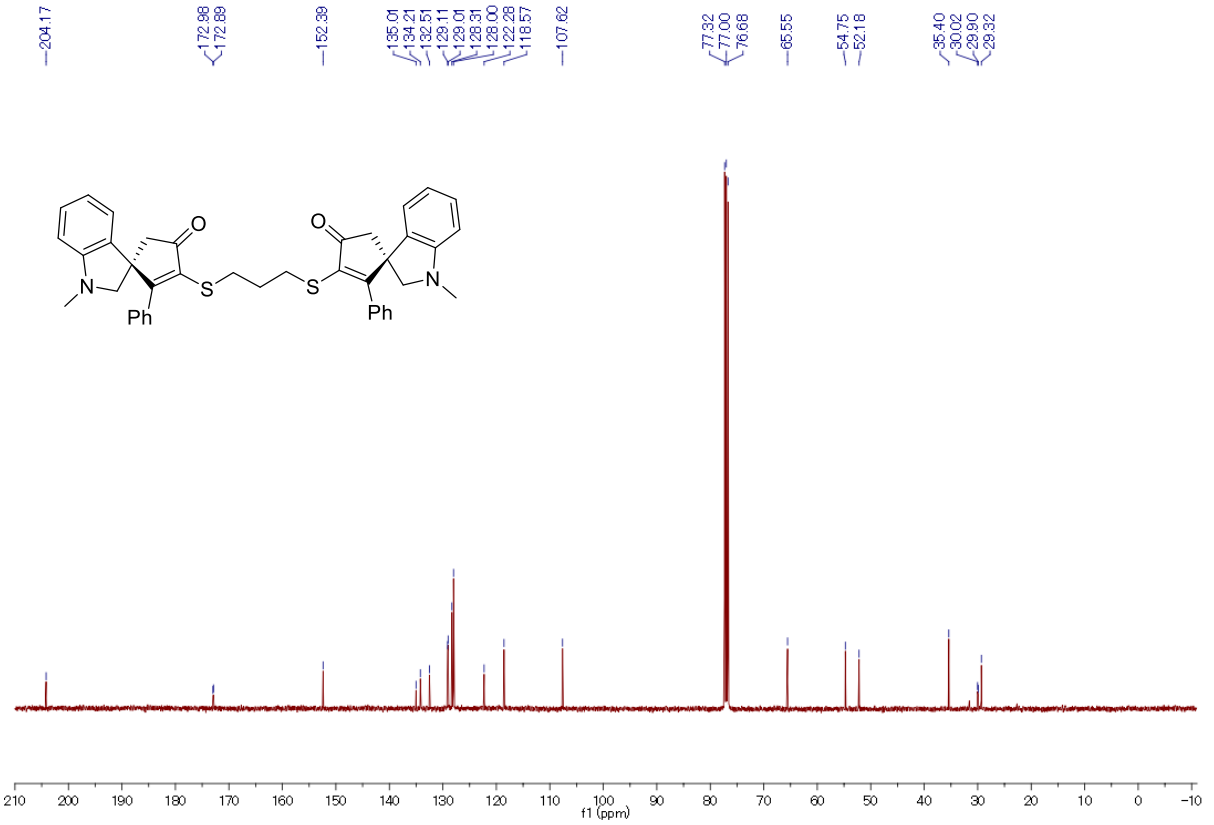
5.88
2.12
6.01
2.06
f1 (ppm)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172.98
172.89
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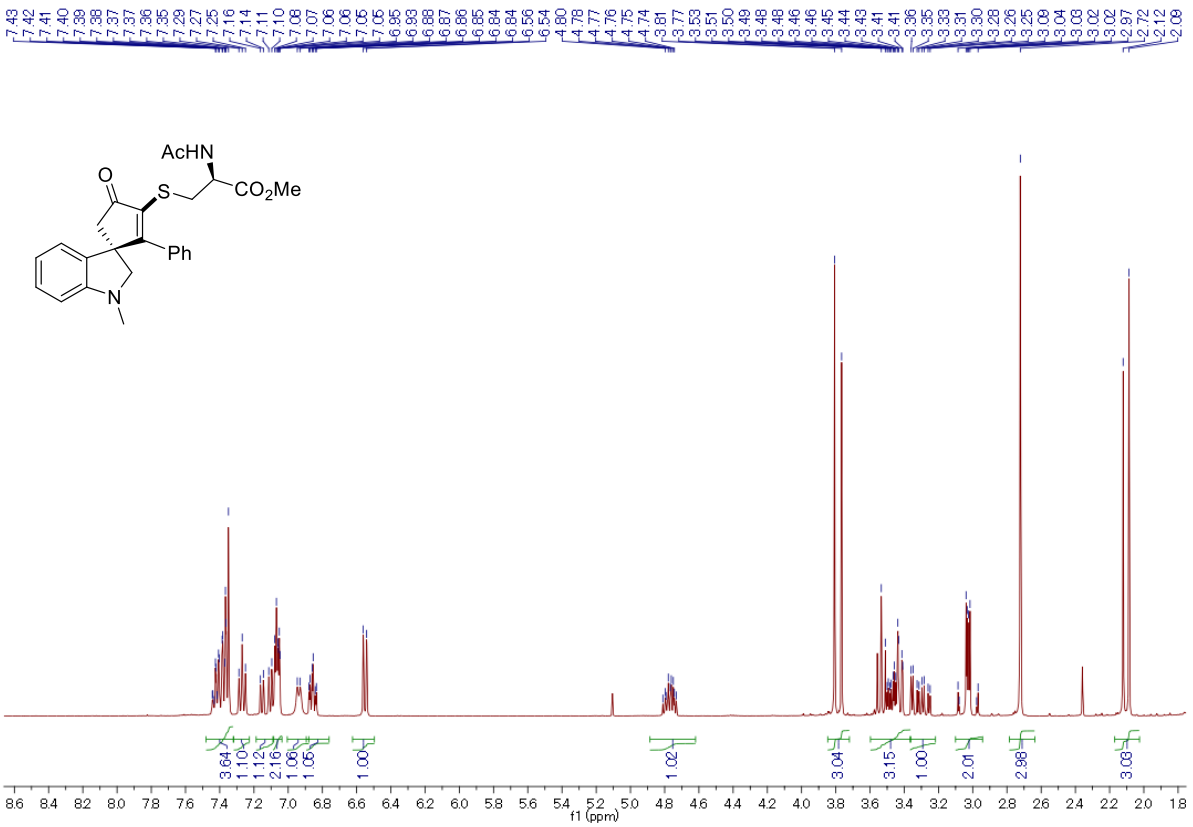
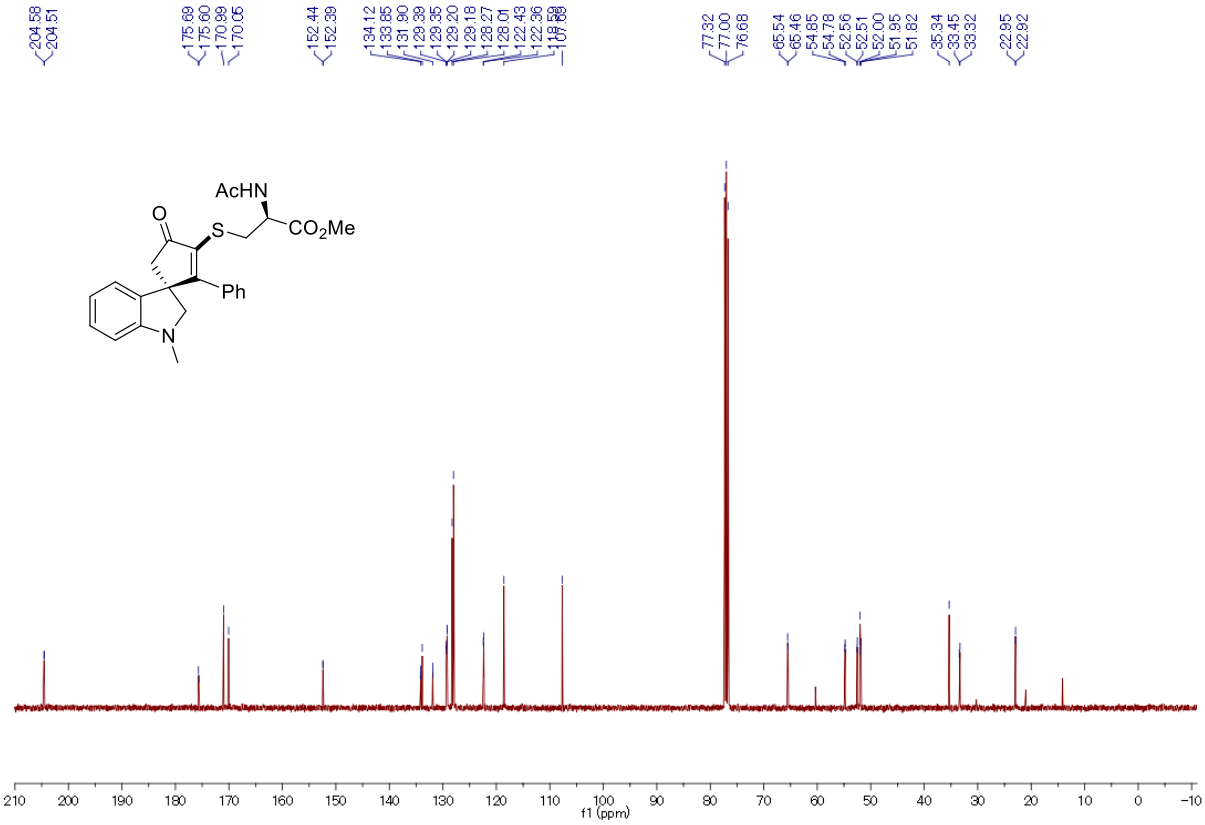
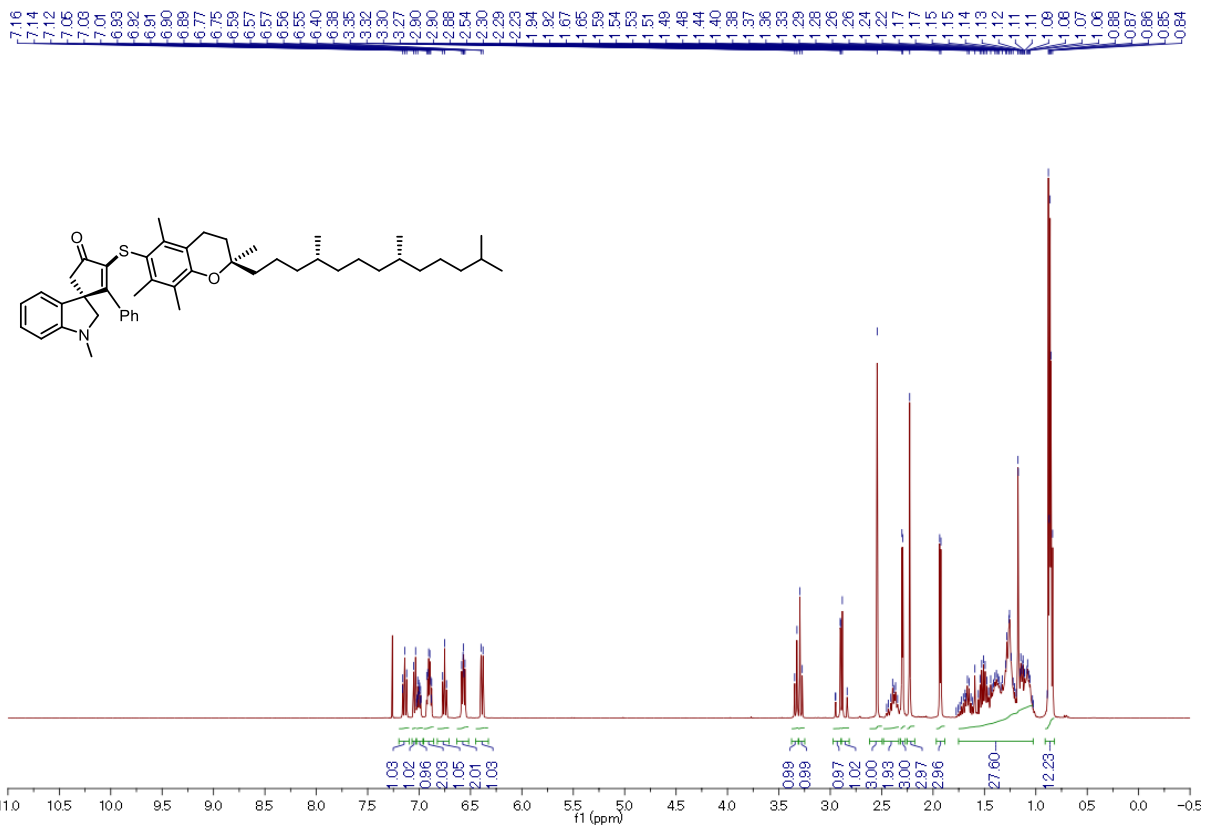
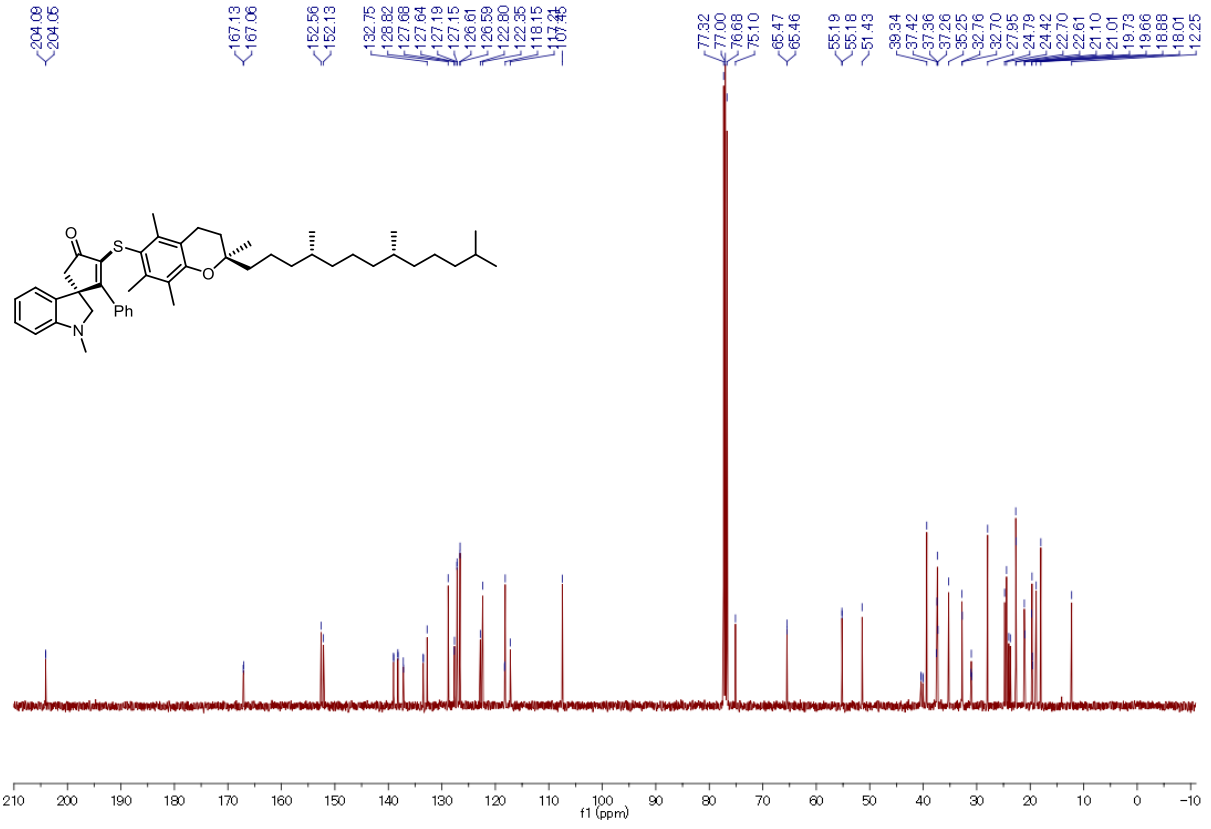
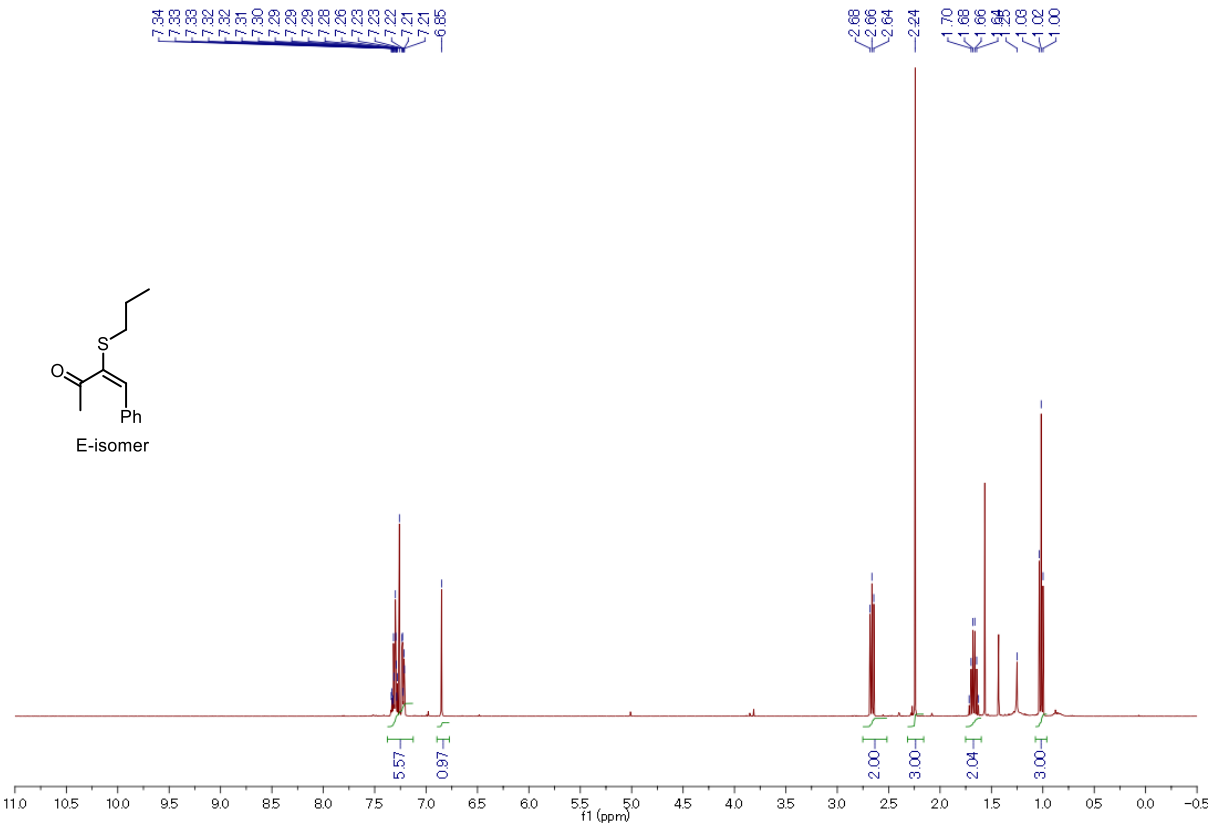
134.21
132.51
129.11
129.01
128.31
128.00
122.28
118.57
107.62
77.32
77.00
76.68
65.55
54.75
52.18
35.40
30.02
29.90
29.32
O
O
S
S
N
N
Ph
Ph
f1 (ppm)

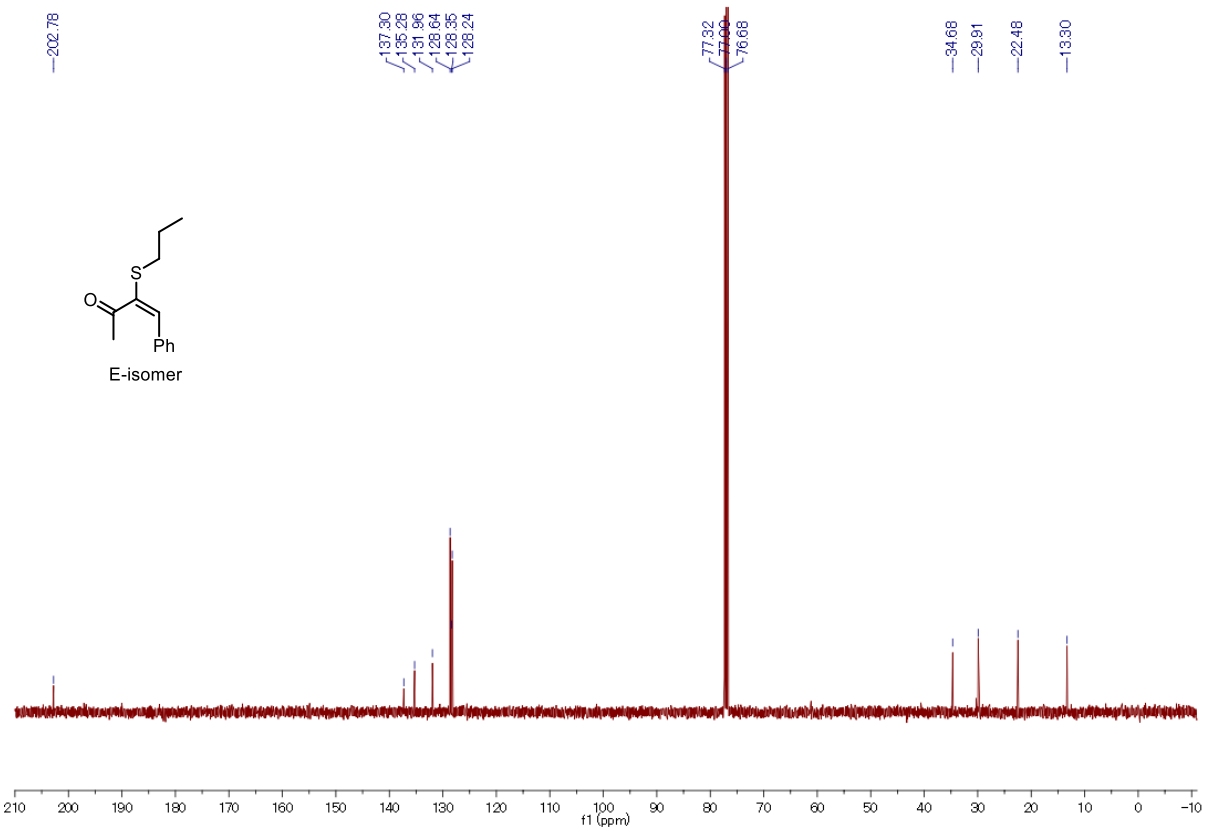

AcHN
O
S
CO2Me
Ph
N
f1 (ppm)

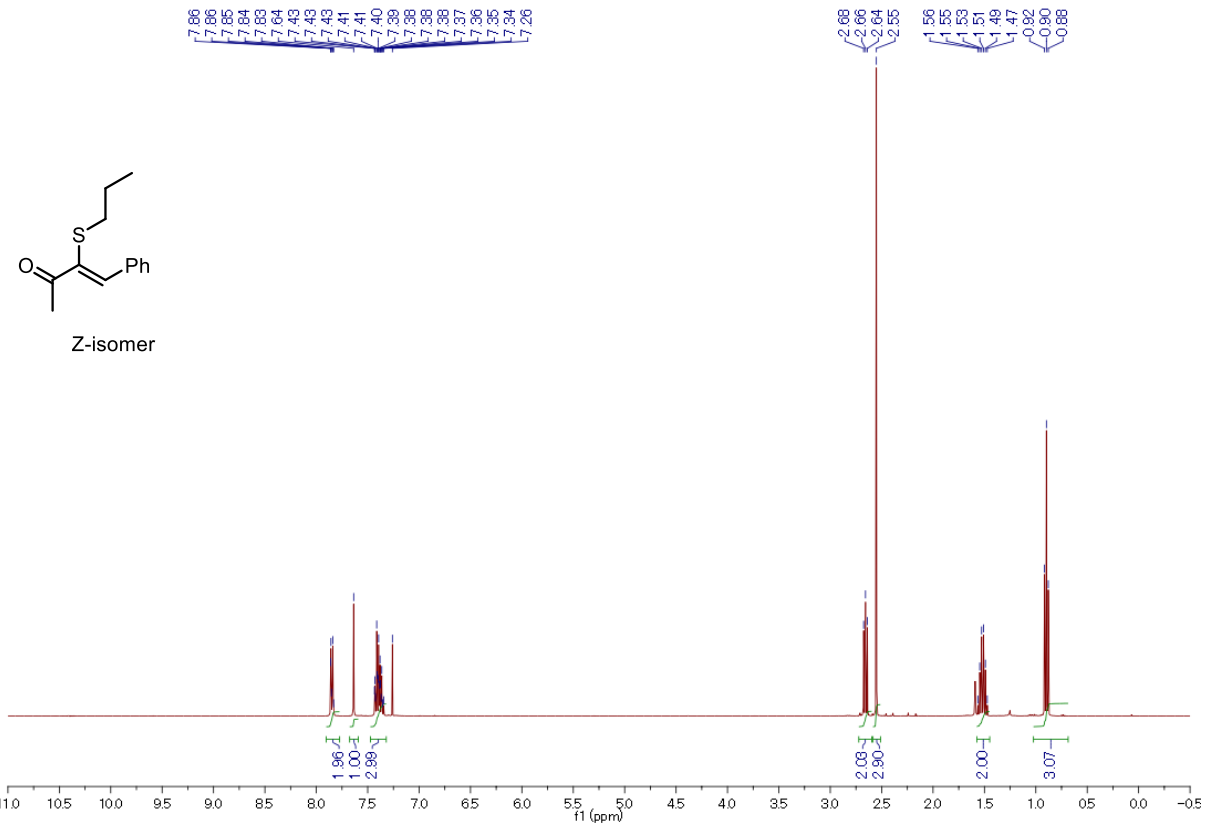

AcHN
O
S
CO2Me
Ph
N
f1 (ppm)


7.16 7.14 7.12 7.05 7.03 7.01 6.93 6.92 6.91 6.90 6.89 6.77 6.75 6.59 6.57 6.57 6.56 6.55 6.40 6.38 3.35 3.32 3.30 3.27 2.90 2.90 2.88 2.54 2.30 2.29 2.23 1.94 1.92 1.67 1.65 1.59 1.54 1.53 1.51 1.49 1.48 1.44 1.40 1.38 1.37 1.36 1.33 1.29 1.28 1.26 1.26 1.24 1.22 1.17 1.17 1.15 1.15 1.14 1.13 1.12 1.11 1.11 1.09 1.08 1.07 1.06 0.88 0.87 0.86 0.85 0.84
O
S
O
Ph
N
1.03 1.02 0.96 2.03 1.05 2.01 1.03 0.99 0.99 0.97 1.02 3.00 1.93 3.00 2.97 2.96 27.60 12.23
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

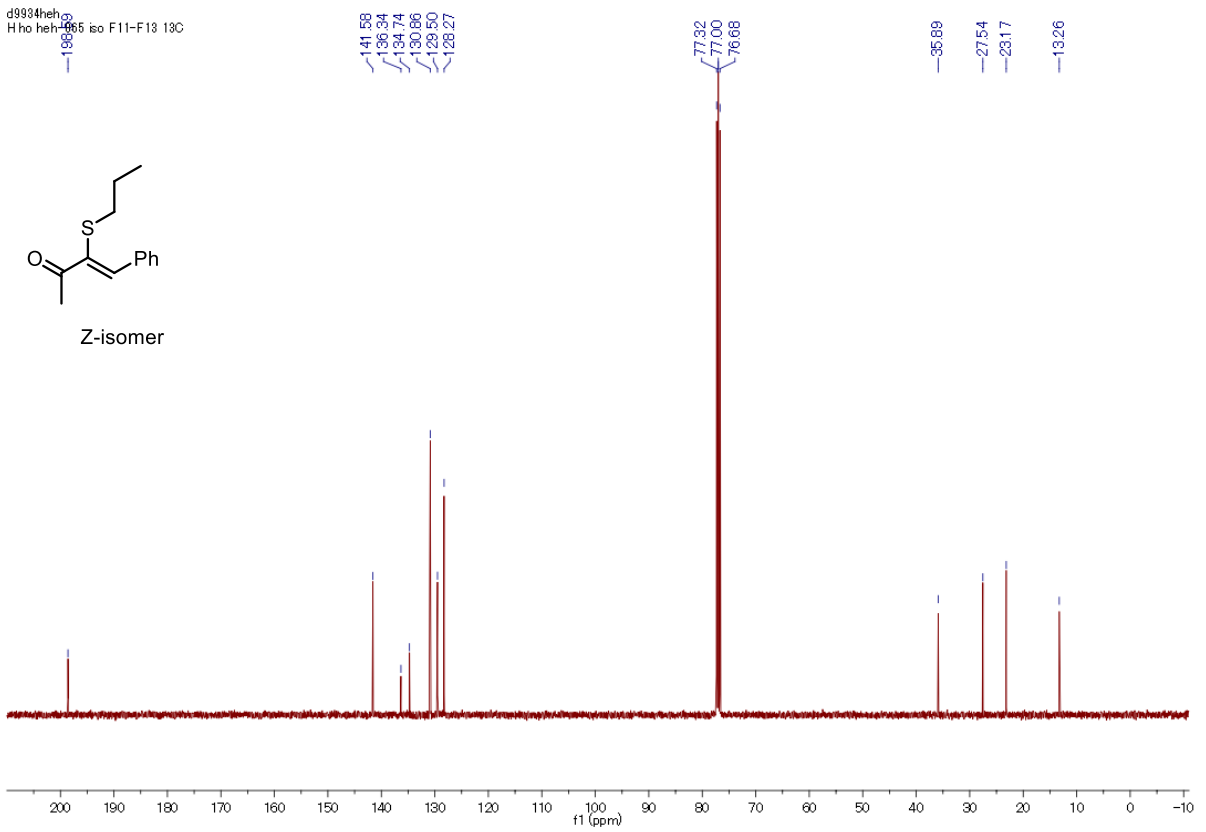

204.09 204.05 167.13 167.06 152.56 152.13 132.75 128.82 127.68 127.64 127.19 127.15 126.61 126.59 122.80 122.35 118.15 117.41 107.45 77.32 77.00 76.68 75.10 65.47 65.46 55.19 55.18 51.43 39.34 37.42 37.36 37.26 35.25 32.76 32.70 27.95 24.79 24.42 22.70 22.61 21.10 21.01 19.73 19.66 18.88 18.01 12.25
O
S
O
Ph
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.34
7.33
7.33
7.32
7.32
7.31
7.30
7.29
7.29
7.29
7.28
7.26
7.23
7.23
7.22
7.21
7.21
6.85
2.68
2.66
2.64
2.24
1.70
1.68
1.66
1.64
1.44
1.03
1.02
1.00
S
O
Ph
E-isomer
5.57
0.97
2.00
3.00
2.04
3.00
f1 (ppm)


202.78
137.30
135.28
131.96
128.64
128.35
128.24
77.32
77.00
76.68
34.68
29.91
22.48
13.30
S
O
Ph
E-isomer
f1 (ppm)

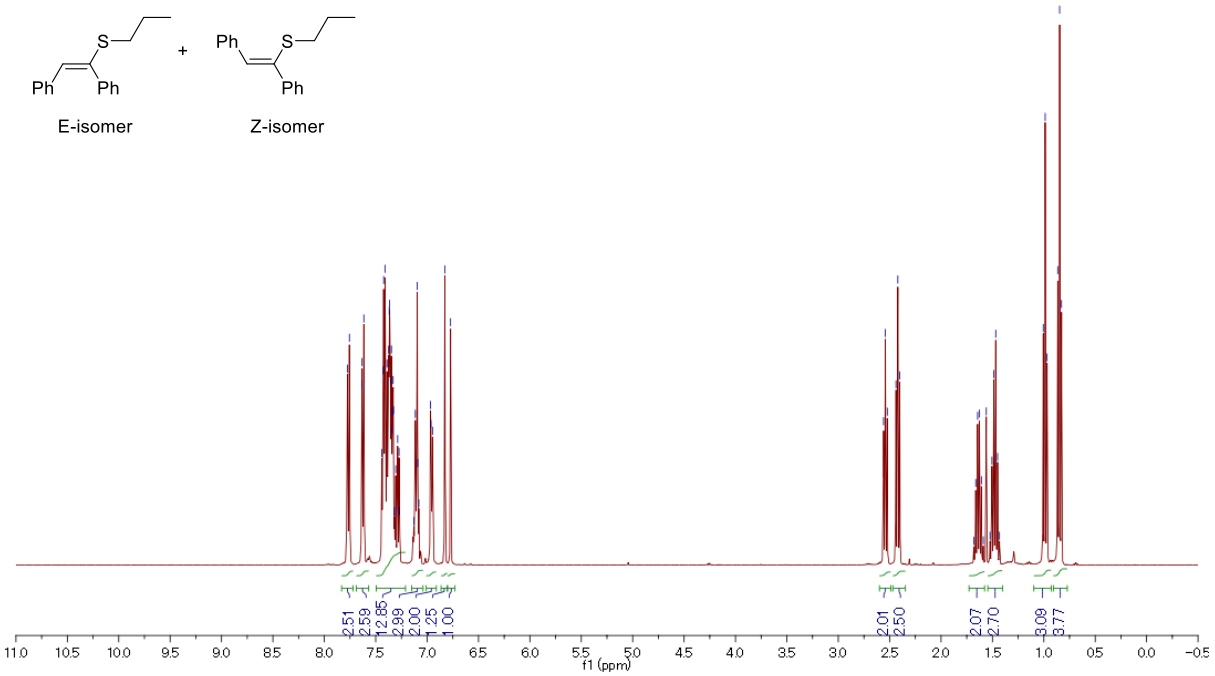


Z-isomer



Z-isomer


7.77
7.76
7.64
7.63
7.62
7.44
7.43
7.42
7.41
7.39
7.37
7.37
7.36
7.36
7.35
7.34
7.34
7.33
7.33
7.32
7.30
7.29
7.27
7.27
7.13
7.11
7.10
7.09
7.08
6.97
6.96
6.95
6.83
6.77
2.56
2.54
2.52
2.44
2.42
2.40
1.64
1.63
1.56
1.49
1.47
1.01
0.99
0.97
0.86
0.85
0.83


S
Ph
Ph
+
Ph
S
Ph
E-isomer
Z-isomer
2.51
2.59
12.85
2.99
2.00
1.25
1.00
2.01
2.50
2.07
2.70
3.09
3.77
f1 (ppm)


141.22
138.33
138.11
137.80
137.10
136.80
131.92
129.59
129.55
128.84
128.57
128.30
127.99
127.95
127.93
127.76
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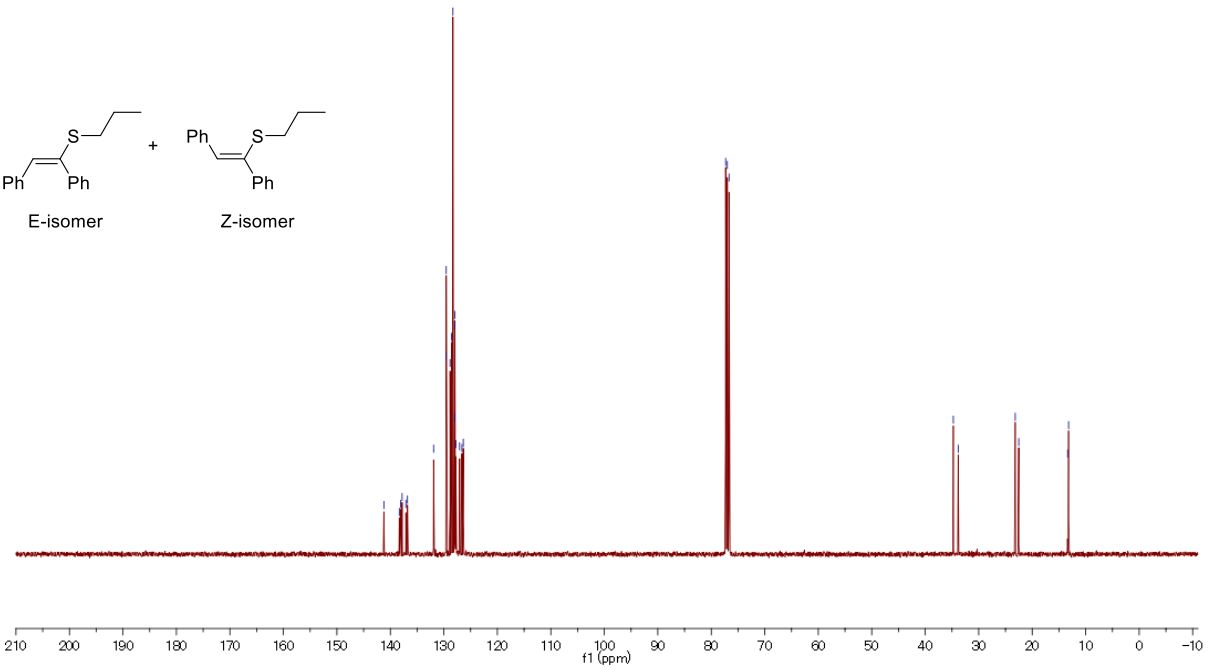
34.75
33.83
23.17
22.52
13.38
13.20


S
Ph
Ph
+
Ph
S
Ph
E-isomer
Z-isomer
f1 (ppm)